SCIENCE FOR EVERYONE

B. I. SREBRODOLSKY

MYSTERY OF MINERALOGY

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Б. И. Сребродольский

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Mystery of Mineralogy

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Preface

The world of minerals, with its diversity of forms, colours and properties, is captivating. Its effects on our life are enormous. Since the beginning of time, humankind has found applications for stone: it was used to build houses, erect monuments, and make arms, tools, and even "books", which allowed information to be passed on to the generations that followed. Throughout the world and in all ages minerals have been participants in wonderful events, beliefs, myths, and scientific discoveries.

Mineralogy is a fundamental science; concepts about the origin of mineral deposits can be based solely on the information provided by this science. This book is the result of many years of the author's studies on an interesting mineral assemblage in sulphate-carbonate rocks. It is intended for geologists, students, and lovers of stones. The basic concepts about solid mineral materials, symmetry and its elements, single crystals, intergrowths and twins, and habitual and simple crystallographic forms, which manifest themselves both in the outward appearance and in the internal atomic structure of minerals, are presented in this book.

The properties of each mineral reflect a specific physicochemical environment and, accordingly, the geological processes that took place at the time of its origin in that segment of the Earth. The determination of these properties may provide a clue to understanding the environments and origins of minerals.

Each mineral has its own history, and the investigator is interested, as an historian, not in its perfections but in its deviations from the norm. The book concentrates on precisely such abnormal crystals, which are invariably puzzling to the scientist. It is significant that they provide valuable information not only about the mineral itself but also about the physicochemical properties of its environment.

Mineralogical investigations form the basis for solving practical problems in the search for minerals. Hence this work addresses not only the characteristics of minerals but also their possible application in geological projects.

Nature is generous with ultimate results but stingy in providing explanations. The investigator, therefore, has to work hard and spend much time in order to reveal the relationship between the mineral and its environment from the origin of the former to its disappearance.

Thus, an interest in the processes occurring in the Earth's crust during which minerals are formed is natural. The book deals with the problems connected with the specifics of calcium sulphate conversion to sulphur and calcite.

Throughout its history humankind has been eager to disclose the secret of the origin of minerals — the marvellous flowers of the Earth — to reveal in greater details their composition and properties.

The beauty of minerals, their shape, colouration, internal pattern, and other characteristic features are not a casual caprice of Nature but a vivid manifestation of the close connection of matter with a specific geological environment.

The esthetic aspects concerning the value of minerals are well known and diverse minerals with esthetic value have long since been used widely as building materials to decorate the interior and the external facings of many architectural masterpieces. Recently, minerals have been extensively studied owing to the application of sophisticated analytical techniques.

The concepts of plate tectonics elaborated both in this country and abroad have fruitfully affected this work. The better the tectonic knowledge of the region, the more prominent and diverse the manifestations of its mineralogical and geochemical specifics appear to be. Obviously, this explains, to a large extent, the fact that the production and proved reserves of valuable minerals are essentially restricted to a few major and unique deposits.

The main factor contributing to progress in any science, including mineralogy, is new ideas. This book, in particular, elaborates the concept of protominerals, which were studied by the author.

The investigator must still be able to be astonished, otherwise there will be little that he or she can see in nature. All minerals are interesting; each is beautiful and mysterious in its own way. An unsightly chalcedony nodule is hardly likely to attract attention, but once you cut it into smaller pieces and polish it, a neat and distinct pattern will reveal itself whose very contemplation will bring you joy. A cold bluish flicker will flow, as it were, from the stone, which was greyish and unattractive before this discovery.

At every step at a sulphur deposit you can see beautiful minerals. These are bright yellow sulphur crystals sprinkled, as if by snow, with powdery calcite. There is calcite overgrown by barite crystals resembling the petal of flowers. Nearby may be a lacy tangle of transparent gypsum plates; a wondrous twinkling light is emitted by a little prism of rock crystal.

The world of minerals is magnificent and unique. It has taken many thousands, even millions, of years for Nature to create these minerals. Some of the puzzles, held by these mysterious creatures of Nature, have been solved, others have not. They are the subject of this book.

Contents

Why Are the Egyptian Pyramids So Long-Lived?

The minerals gypsum and anhydrite, barite and celestite, whose wonderful properties have been amusing man since times immemorial, are still subjects of keen interest to various investigators. Scientists are also eager to know why stone is so resistant to weathering.

Gypsum and Anhydrite

Gypsum and anhydrite are evaporite minerals similar in chemical composition, but gypsum contains water while anhydrite does not. This is even reflected by the name: anhydrous stands for the Greek *waterless*.

Gypsum and anhydrite are common in the upper Earth's crust, in sediments as old as Cambrian and younger. They frequently constitute layers and lenses in limestones, dolomites and rock salt. In nature, these minerals are confined to rather definite depths. Anhydrite mainly occurs deeper than 460 m from the Earth's surface, and gypsum at shallower depths. Under common atmospheric conditions, anhydrite vigorously absorbs moisture and gradually over time converts to gypsum. This is accompanied by a substantial expansion of the rock, which often causes its crumpling and fracturing. For this reason many mining openings running through rocks containing anhydrite beds are disturbed.

The geologist V. Zverev describes two major ways of anhydrite to gypsum transition. Groundwater circulation along horizontal fractures gives rise to a bed-by-bed banded texture of gypsum. When water penetrates through an anhydrite bed in a capillary fashion, dotted or stellular form of anhydrite hydration arises.

Experiments in the laboratory at the Kungur Station, Ural Branch, USSR Academy of Sciences, have confirmed that gypsum dissolves much more rapidly than anhydrite. Gypsum solubility is different in different salt solutions, being most intense in water containing relatively much sodium chloride and sulphate. It rises to some point and then falls, owing to a so-called desalting effect. Gypsum with impurities dissolves faster than its pure varieties.

The origin of gypsum and anhydrite has long been under heated discussions. As noted, gypsum occurs at outcrops of sulphate rocks and gradually gives way to anhydrite towards the deeper parts of the mass. It forms, as it were, a weathering crust of anhydrite, the hydration degree of the latter depending directly on its fracturing extent. This suggests that the sulphate initially laid down in ancient water reservoirs was anhydrite. But detailed studies into sedimentation in modern water reservoirs and experiments on sea-water metamorphism have shown that the sulphate deposited in ancient reservoirs was gypsum. According to experiments, gypsym is laid down from solution at temperatures below 42 °C, whereas anhydrite at higher temperatures.

Crystalline gypsum precipitated in isolated sea embayments. For it to settle down on the floor of a basin, approximately 40 per cent of water must evaporate (one litre of water produces 1.3 g of gypsum). Stronger evaporation triggers precipitation of rock salt with calcium and magnesium sulphates; finally, potassium and magnesium chlorides and sulphates are laid down, accompanied by rock salt. This means that each dissolved salt can crystallize from saturated solution only under certain conditions.

An important property of gypsum is that it loses water on heating to convert into alabaster. Being mixed with water to produce a kind of dough, alabaster heats up and solidifies very rapidly. Thanks to this property, gypsum is widely used for plaster, in architecture, and in making models, copies, casts and dentures. Alabaster powder is used in surgery; mixing with water produces paste that is spread over bandages.

Gypsum is also a binder, and its compact varieties are used to make various articles, such as little figures and decorations. Especially good for this is selenite — parallel-fibrous gypsum of warm tinges with a twinkling, playing and yellowish lustre, like that of the Moon (Greek's Selena), shot with mother-of-pearl and silk. One of the old engravings of 1497 shows selenite as droplets of the lunar foam falling onto the Earth.

Since ancient times, gypsum has been known as a binder. The Egyptians used it in erecting pyramids 3 000 years B.C. The huge blocks in these pyramids are bound up with a gypsum slurry that has been proven to be exceptionally strong. Sunlit hot, fanned by burning wind, the pyramids are 50 centuries old, and their gypsum cement is becoming stronger and stronger rather than breaking down. In the antique world, gypsum was widely utilized in manufacturing art and household articles, erecting monumental constructions. In Old Russia, the period of exploitation of gypsum deposits (12th-13th centuries) coincided with the start of an extensive gypsum application for construction purposes. A gypsum binder was, for instance, used by builders of the past when they constructed the Golden Gates in Kiev.

As early as 2 000 years ago, North American Indians put gypsum into salted soils as a fertilizer. They believed that this snow-white stone is a symbol of luck and wealth. Near the present-day town of Herakleon on Crete Island, preserved are remains of the palace of Minos gold culture developed in the 3rd to 2nd thousand years B.C. All floors of bathrooms, halls and other premises in it are made out of gypsum. The Ukrainian gemmologist V. Suprychev reports on the "rock crystal" town of Risafa recently found by archaelogists in the Syrian Desert. The town is located on an artificial hill. Crystalline gypsum plates make up fortress walls, a temple and other buildings. In Ancient Rome, light-coloured anhydrite, called vulpinite or bergam marble, was a common material of columns and building decoration.

Alabaster is cryptocrystalline snow-white gypsum, translucent and dense, similar to marble, often with a lovely pattern of differently coloured veinlets and patches. Its name is derived from the ancient Egyptian town of Alabastron at the outskirts of which alabaster has been mined since long ago. Like marble, it can be carved easily. Statuettes, illuminants, vases and vessels for oil and aromas have been made out of it since old times. The beauty of alabaster is due to its tender-yellow tinge and a graceful pattern of wavy veinlets and patches. The stone is beautiful, not in large blocks but in thin-walled articles, when sunlight or mild candle light passes through them. Because of this, alabaster bowls and vases are usually placed at the window.

Alabaster vessels are frequently found by archaeologists. They were encountered in the famous Tutenkhamon tomb. This tomb also contained a goblet in the form of a lotus flower made of translucent alabaster. An alabaster vessel with the sign "Artaxerxes, Pharaoh the Great", made in Ancient Egypt, was found in 1971 in a burial-mound on the bank of Kumachka River, Southern Urals. Artaxerxes reigned in 465-425 B.C. Alabaster vessels were dug up within Bosporian Panticapaeum and Sarmatian burial-mounds in Prisivash'e, Crimea.

The Renaissance Age witnessed a true blossoming forth of art carving on alabaster. Decorative alabaster has been used until now in the town of Volterra, near Pisa, Apennines foothills, to make very fine vases, flower pots, lustres, lamps and other articles, occasionally even whole columns.

In Russia, manufacturing handicraft ware from gypsum (selenite and alabaster) and anhydrite was greatly developed late in the 18th century. Very popular were articles cut out of selenite by handicraftsmen of the Perm Region. A stone-cutting mine arose at the Kungurskoe deposit. These objects, made out of Perm selenite, were shown at the Russian Handicraft Wares Exhibition in St. Petersburg in 1913. Those made at the *Ural Stone Cutter* Factory are now in high demand both in our country and abroad. It is exported to 40 countries.

Alabaster wares are saved in many museums. The Pushkin Art Museum in Moscow exhibits a splendid narrow-throttle, thin-walled vase about 1 m high, cut out of a massive block of translucent alabaster in the third millenium B.C. Beautiful alabaster cups and vases cut out by Italian artists (the second half of the 18th century) are shown in the Paul Palace, now a museum, near Leningrad.

Gypsum and anhydrite uses are now quite diverse. Gypsum is calcined and milled to produce not only paster alabaster but also sculpture, or mould gypsum. Such gypsum is easy to process, grind and polish. The addition of gypsum to cement improves the quality of the latter; the result is Portland cement whose binding properties allow it to be used even under water.

This country contains large gypsum reserves that cannot be used in construction. Experiments in the city of Gorky have shown that such gypsum can readily be converted to decorative material not worse, sometimes even better than marble. Also, artificial marble is one and a half time cheeper than natural marble of a similar colour.

Wonderful curved (pod-like) crystals of gypsum are rather common, but their origin has found no satisfactory explanation. These crystals are generally located in clay. They range here from small crystals to intergrowths some 10-15 cm across. Curved crystals from different mineral deposits are geometrically nearly identical.

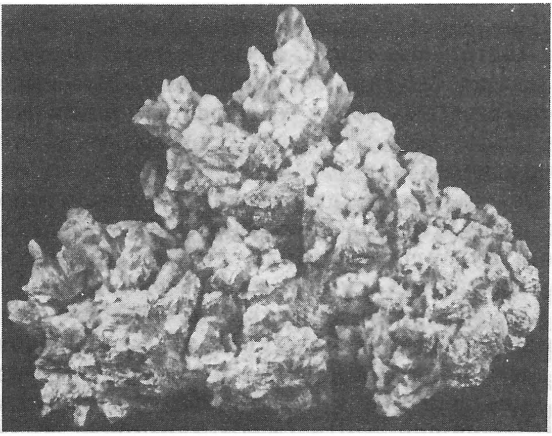
The pod-like shape of crystals is due to preferential development of the face of rhombic prism {111}, which becomes curved during its growth. Concentrating crystallization of dispersed calcium sulphate in the clay produces the gypsum crystals described here. Because of its crystallization pressure, the growing gypsum pushes back clay particles that hamper crystal growth.

The origin of curved crystals was studied by the French scientist G. Deicha. He paid attention to the fact that curved faces of some crystals can be resolved into many planar unit faces. His experiments have shown that curved faces can be accounted for by the presence of sodium chloride in the mother liquor. With the increasing salt concentration, gypsum individual crystals are becoming more and more curved.

Curved gypsum crystals are rather widespread in the gypsum belt of the Ciscarpathians. If we adhere to Deicha's viewpoint, then it is unclear why these crystals occur together with common (fully faced) gypsum crystals. Moreover, some white spar gypsums contain curved brown crystals of the same mineral. How can such different gypsums form under identical conditions? This is puzzling.

Curved gypsum crystals in clayey rocks frequently produce intergrowths looking like flowers; that's why they are called gypsum roses. In loose sand masses, gypsum does not push back sand grains but absorbs them during its growth. This is so-called Repetek gypsum.

Mysterious are banded gypsums. They have been found very recently in some karst caves of Soviet Central Asia. Crystals are up to 1 m long, 1.5 cm wide and first few millimetres thick, and grow only on the floor of caves. They are pure and transparent, and



Druses of gypsum crystals

have a wavy habit face (probably {010}) because they inherit irregularities of the substratum while spreading over the uneven cave floor. Apart from banded single crystals, their tabular-diverse aggregates resembling white felt were noted. The crystals that are disconnected with the substratum become feculent.

How do the banded gypsum crystals originate and grow? It cannot be ruled out that some chemical elements play certain part in this.

Puzzling is the fact that gypsum is easily replaced by many minerals to form pseudomorphs. These retain the crystallographic shape of separate grains or aggregates of the host. Pseudomorphism implies chemical selectivity of replacement, volume preservation during replacement and adherence to other basic rules of this complex process. The formation of pseudomorphs is a major distinctive feature of epigenetic (superimposed) mineralization.

Many minerals in sulphur deposits form pseudomorphs after gypsum and anhydrite — the basic source of native sulphur in sedimentary rocks. They provide substantial information about genetic processes in individual crystals.

That sulphur can replace gypsum has been known for a long time. Pseudomorphs of sulphur after selenite — parallel-columnar gypsum — are common in many deposits. The replacing sulphur is fine-grained, and its structure is the same as that of selenite. Granular sulphur replacement after curved gypsum crystals is widespread in the Ciscarpathians. It is first spread along fissures and cleavage joints and gradually extends to embrace the whole crystal. Radial-fibrous pseudomorphs of sulphur after gypsum with relics of anhydrite grains have been found deep in the Ciscarpathian mineral deposits.

Calcite pseudomorphs after gypsum have been noticed in sulphur occurrences in the Kerch Peninsula. Calcitization has involved gypsums of the Chokrak Bed. The bed with the pseudomorphs is as thick as 2 m, and it contains not more than 50% calcite. The calcite inherits details of the internal structure of rhombic gypsum grains. In the ores of the Syrian deposit, the calcite replacing gypsum, which in its turn is an anhydrite hydration product, occurs as lamellae and radial-fibrous aggregates.

Pseudomorphs of sulphur and calcite after gypsum look like gypsum or anhydrite, depending on the host mineral. They are common in the sulphur occurrences in Kerch. The shape, size and location of pseudomorphs are similar to those of gypsum in primary (sedimentary) beds. In some places of the Ciscarpathians, sulphur and calcite replace columnar gypsum crystals enclosed in sulphur. The newly formed sulphur is nearly the same as that of the earlier generation. Gypsum has left behind only its outlines clearly marked by calcite.

Pseudomorphs of calcite after anhydrite as rod-like crystals untypical of calcite have been found in the Ciscarpathians. In the Dernovo-Milyatin (Lvov Region) sulphur occurrence, calcite forms incomplete pseudomorphs after anhydrite at a depth of about 1 700 m. Here also, sulphur pseudomorphs after anhydrite have been found on very rare occasions in the ore. Sulphur replaces anhydrite along cleavage joints extending in three directions.

Pseudomorphs of sulphur and calcite after well-crystallized anhydrite are of importance in the sulphur ores of the deposit in Syria. Note that the American scientist R. Taylor denied direct replacement of anhydrite by a sulphur ore. He attributed this to the fact that the conversion of anhydrite to gypsum is much faster than anhydrite replacement by sulphur and calcite. Sulphur and calcite spread along cleavage joints in anhydrite. Sulphur was noticed along the plane (010) of anhydrite and calcite perpendicular to it on the pinacoid plane (001).

Celestite pseudomorphs after gypsum are observed in the ores of the Ul'kun-Burultau (Kirgiz Soviet Socialist Republic) and in some deposits (Syria). The replacement proceeds along very perfect cleavage joints in gypsum. The newly formed celestite, in its turn, is replaced by calcite and gypsum (selenite). While the celestite contains relics of gypsum and anhydrite grains, the sulphur and calcite replace only gypsum. If anhydrite relics are only present, incomplete pseudomorphs of calcite after celestite are generated.

Barite pseudomorphs after gypsum are characteristic of ores in the Ul'kun-Burultau deposit. The replacing barite occurs in small aggregates, has a fan-like extinction, and contains abundant relics of anhydrite transformed into gypsum; like celestite, it spreads along very perfect cleavage joints.

Quartz-after-anhydrite pseudomorphs have been found in sulphurated gypsums of the Ul'kun-Burultau sulphur occurrence. The sulphate nodule wholly replaced by quartz have a poikiloblastic texture due to relict anhydrite. The quartz may have originated not after anhydrite but after calcite, and then it inherited the anhydrite present in the calcite.

Pseudomorphs of pyrite after gypsum have been noticed in limestones from Kerch sulphur occurrences; they are rhombic, which is unlike calcite.

Common in sulphur deposits are sulphur and calcite pseudomorphs after irregular gypsum and anhydrite grains. They are nearly indivisible in a fine-grained sulphate rock entirely replaced by a sulphur-calcite aggregate.

The structure of pseudomorphs occasionally reflects stages of mineral formation, as seen in so-called double pseudomorphs. The gypsum porphyroblasts in them are first replaced by calcite and then by sulphur with the preservation of the morphology of the initial sulphate. All pseudomorphs are of the same age. The host mineral alters simultaneously with the input of a newly formed mineral. Besides the pseudomorphs after gypsum and anhydrite, the sulphur clearly replaces barite and celestite.

All this supports the postulation that sulphur tends to produce pseudomorphs after sulphate minerals, which ultimately leads to formation of sulphur ores. This shows that sulphur is settled down by stages.

It is not quite clear how anhydrite as a product of gypsum dehydration is formed in a very acid environment present in the oxidation zone of some deposits. It was taken earlier as a semihydrate of calcium sulphate ($CaSO_4 \times 0.5H_2O$) that arises in a dry desert climate. Experiments on a 22% sulphuric acid solution proved somewhat later that gypsum is converted to anhydrite rather than to calcium sulphate semihydrate. That's why we were more inquisitive to the gypsum oxidation products in oxidized sulphur ores.

Detailed examination of gypsum from the surface zone of the Gaurdakskoe deposit, Turkmen Soviet Socialist Republic, has shown that its dehydration products consist of anhydrite and relict gypsum. At the Vodinskoe deposit, selenite-like gypsum veinlets transformed into anhydrite cut across weathered sulphurated limestone in the central area. In the oxidized ores of the Giik-Salganskoe sulphur occurrence, the anhydrite occurs in thin crusts, stellar intergrowths, and complete and incomplete pseudomorphs after gypsum crystals. The thin anhydrite crusts are easy to scrab off the crystals to expose fresh water-transparent gypsum. Anhydritization starts at crystal faces and gradually involves the whole gypsum crystal. The intensity of gypsum dehydration with the formation of anhydrite is controlled by the pH of the environment. At a pH about 4, incomplete replacement pseudomorphs are noticed; at a $pH \leqslant 2$ essentially the whole gypsum is transformed into anhydrite. Considerable concentrations of anhydrite in the oxidation zone of the Giik-Salganskoe sulphur occurrence have been found at the surface below the outline of the sulphur body, under the obviously secondary, fine-grained gypsum masses. The secondary anhydrites of the deposit are of various forms in Syria.

Anhydrite is invariably found in evaporites that make up salt domes. It is observed there as somewhat imperfect crystals ranging in size from fractions of a millimetre to 2 mm. Grains of the mineral concentrate in so-called annual layers, rather than being dispersed in the salt. The amount of anhydrite in the layers varies between 4 and 90%. The anhydrite contains intergrowths of fine dolomite, quartz, pyrite and sulphur grains, concentrations of carbonate and carbonaceous material, gas bubbles, and liquid drops. The anhydrite percentage increases upwards in the salt unit.

Well-defined anhydrite crystals are rather rare. Minute sulphates are tabular or rod-like.

In our collections, the anhydrite occurred as polyhedra only at two places: in the Dernovo-Milyatin region, Volyn-Podolsk end of the East European craton, at depths of 1736-1780 and 1787-1789 m, and in the Novosanzharskii salt dome, Dnieper-Donets depression, at a depth of 1 029 m. It lines small cavities in sulphurated sulphate-carbonate rocks. Anhydrite crystals are dipyramidal, well outlined, and are as large as 2 mm. Their habitual dipyramidal faces are covered with dense horizontal striations. Yellow sulphur fills interstices between anhydrite crystals and frequently preserves at its surface imprints of sculptural figures typical of anhydrite faces. At places, the anhydrite is distinctly replaced by sulphur and calcite.

Barite

Barium is rather widespread in nature. Its content of the Earth's crust is 0.05%, which is fairly high, higher than, say, lead, tin, copper, and mercury. The main barium mineral barite has been known since the 18th century. It is among rather common minerals of the Earth's crust.

Barite had not found commercial application until the middle of the 19th century; it accumulated in tailings left behind after barite-bearing ore processing to extract gold, rare metals, copper, lead and zinc. Barite found its first industrial application in the

1880s, namely in chemical and paint and varnish industries. In the 20th century, barite was utilized in petroleum, rubber, leather, paper, glass, textile and food industries, in nonferrous and ferrous metallurgy, medicine, production of synthetic and construction materials, road building, ceramics and agriculture. Because of this, the production of barite has grown rapidly. It was 0.5 million tonnes in 1913, with half of this amount produced in Germany. The centre of barite production moved from Europe to the USA at the time of World War I. In Russia, barite was first mined at the end of the 19th century, and now it is produced in more than 40 countries. The main resources of this mineral are in the USSR and USA, the USSR being the leader.

The use of barite in modern industries is based on its useful properties as follows: high density, white colour, chemical inactivity and capability to absorb X-rays. The last property is widely utilized in medicine. Barium sulphate is mixed with water and is given to the patient to swallow. Those sections of the digestive tract along which "barium flour" passes are dark on the screen. In this way the doctor obtains information about disturbances in the human body.

Barium is known to be used in more than two thousand manufacturing processes. Two thirds of the barite output is utilized in oil and gas industry while drilling deep wells. Finely ground barite is added to drilling mud, thus making it heavier and thicker, more resistant to gas escape. Barium salts are toxic in any appreciable concentration. They are especially dangerous when they enter into the blood.

Barium mineralization in the Ciscarpathians is restricted to the upper beds of sulphur-bearing limestones. It extends from the overlying clay to a depth of 4 m. Barite is the only ore mineral. Orebodies occur as veins, veinlets, nestles, geodes, and ball- and ellipse-shaped concretions. They stretch for up to 20 m, being not more than 1 m thick. The barium amount in the orebody is decreasing downwards. The barium sulphate concentration is high where the sulphur ore bed is relatively thick. Substantially baritized segments form their own type of barite ores.

Barite phenocrysts range from minute to large idiomorphic, mostly tabular crystals. They are milk white, grey, light brown, or colourless. Brown tinges are most common; they produce zones in crystals. Many crystals have a bog iron ore “jacket”. The massive barite varies in texture between finely and coarsely crystallized, being generally coloured grey or light grey.

The brown barite is more similar in optical properties and density to the barium sulphate than to the colourless and milk-white barite.

In the Razdol'skoe deposit (Ciscarpathians), barite occurs in several generations. The first is disseminated barite — transparent columnar crystals up to first few millimetres long.

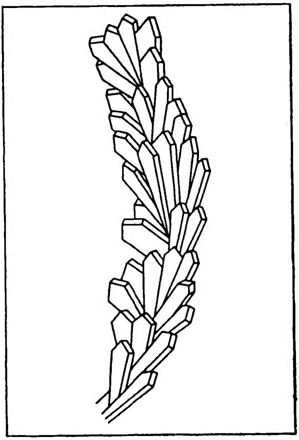
They have the following simple forms: {001}, {110}, {011}, {010}, {104}, {102}, {101}, {100}, {111}, {112}, {120}, {122}. The faces are smooth and bright, nearly "ideal".

The second barite generation is observed in geodes and concretions, and as peculiar stalactite-like, stem-like and spiral forms. All of them consist of tabular crystals, up to 1.5 cm, on (010). Many crystals that line geodes are zoned. These zones were once the outer surface of the crystal; they reflect certain stages in its growth and are frequently pigmented with brownish matter. The zoning is either contrasting, with a clear-cut boundary between zones, or non-contrasting, with a gradual transition, occasionally clearly asymmetric. One can observe an intermittently closer spacing of very thin zones on some crystals (this points to a relatively slow growth), and broad zones due to a rapid growth.

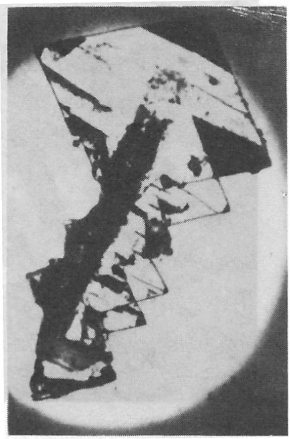
The faces of crystals, especially large ones, are covered with growth layers visible even with a naked eye. When studied goniometrically, such faces yield poor reflections.

Barite polyhedra often form aggregates. A crystalline aggregate is a system of mutually contacting crystals or crystal grains. Stellular barite intergrowths are curious.

Still puzzling is generation of stalactite-like barite aggregates and helictites previously unknown for this sulphate. Stalactite-like aggregates are elongated and are oriented by gravity. They are very similar in outer appearance to stalactites — speleothems formed by crystallization from mineralizers that dropped from the arch roof of a cave leaving behind some of the mineral matter. Contrary to true stalactites, no central channel is present in these aggregates. Its place is occupied by fine-grained calcite to which barite crystals become attached. Hence the surface of the stalactite-like aggregate is not smooth but rough because it is formed by barite crystal apices.

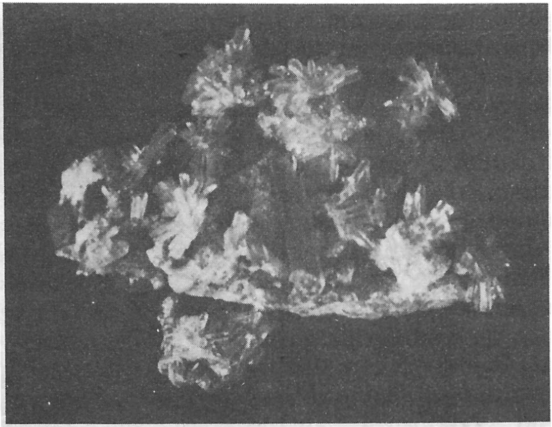


A "branch" of crystals



Intergrowths of barite crystals

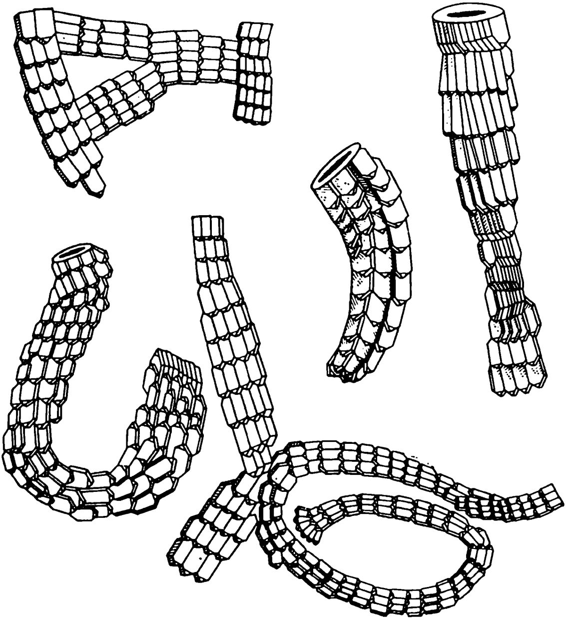
Like typical dropstones, stalactite-like forms hang vertically from the ceiling of a geode or are occasionally attached to its bottom. They undoubtedly mark the direction of gravity and hence can be used as a mineralogical "plumb". These aggregates are cylindrical, not more than 5 cm in length and 0.5 to 0.8 cm in diameter. They are composed of small, well-faced, tabular barite crystals with their x-axes oriented towards the calcite rod. Otherwise small tabular crystal geodes — barite roses — arise. Dendritic barite aggregates grow over the walls of small geodes in sulphurated limestones. These are small (up to 1 cm) mounds and rods of barite with characteristic side branches. Each has



Barite "flowers"

an inside channel from which small fibrous barite crystals radiate. These aggregates are axiolites — forms whose fibers radiate not from one point, as in spherulites, but from a straight or curved line. The role of the channel in the aggregate is not fully understood. In most probability, barite-bearing solutions pass along it. The fibrous barite crystallized from a solution that differed somewhat in composition from that responsible for stalactite-like aggregates.

Interesting are helictites — spyrally twisted forms the growth of which is independent of gravity. Resembling spyralled hooks, they rarely hang from the ceiling of cavities in both sulphurated and non-sulphurated limestones. The central part of each helictite is formed of fine-grained barite with a narrow inside channel up to 3 mm in diameter. The helictite is covered by small (as large as 2 mm) tabular barite crystals with non-identical, though similar, crystallographic orientations. Its growth is the result of finely granular barite crystallization from a solution that passes through a narrow channel, and crystal precipitation from the mineralizer that fills the cavity. The position of the x-axis of each consecutively overgrowing crystal changes progressively and almost never coincides with the direction of its growth. Such wedge-like build-up of crystals leads to a gradual bending of the aggregate and its transition into helictite. It is the preferable crystal growth along the x-axis that twists the aggregate. The crystallization force of growing barite proves to surpass the gravity applied to the mineral.



Spirally twisted forms

The third-generation crystals are tabular on (001). They do not exceed 0.5 cm in size, are bounded by faces, and are colourless or light grey. This barite is overgrown by milk-white, opaque barite. This is the way in which characteristic two-colour crystals arise.

The transparent crystals and their second-, and more seldom third-generation intergrowths are at places covered by fourth-generation barite. These barites contain as much as 1.54% strontium oxide; hence they are called strontium barite — a kind that has not been described before.

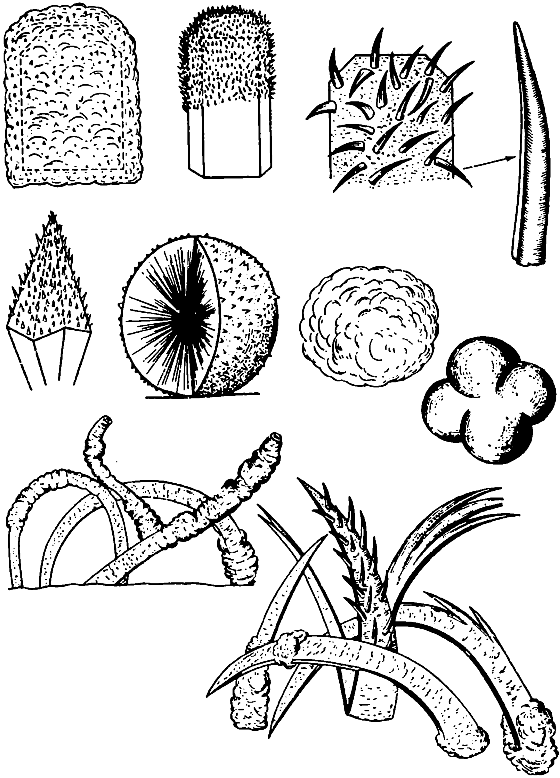
Strontium barite is an enigmatic mineral. It most frequently coats, as a brownish shagreen, colourless tabular barite crystals. The surface of the mineral is rough and is covered with numerous pimples, tenths of a millimetre in cross-section, and acinaci-formed outgrowths projecting in all possible directions and looking like a trick brush. The outgrowths are 1-1.5-mm long and hundredths of a millimetre thick. They are zoned and radial-fibrous in cross-section.

Grey and dingy-grey strontium barites occur in grape-like concentrations — radial-fibrous balls and hemispheres up to 1 mm in diameter. Their surface is covered by miniature spine-like outgrowths. Besides the compact segregations, hollow (skeletal) forms of this mineral have been noted. They occur as small openwork clumps and whimsically curved links and bridges connecting some barite crystals. The mineralogical constants of strontium barite do not differ from those of common barite.

The barite of the fifth generation occurs in skeletal forms. They look rather unusual: case-shaped skeletons and crystal faces grown into the rock and projecting in all directions, rather than common crystals. Small peculiar "boxes" of barite, hollow or filled with rhombohedral calcite crystals grown on box walls, are formed occasionally. The faces (walls) of these boxes are even and bright, the reflections from their inner walls are commonly better than from outer faces.

Barite and celestite occur at different levels in the sulphur-bearing limestone: the former precipitates at the top and the latter, at the base of the unit. It has been found that the chemical composition of these minerals is also a function of their occurrence in the vertical section of the orebody. The higher in the section lies celestite, the higher the content of barium oxide in it; the lower in the section occurs barite, the greater the content of strontium oxide in it. This suggests that the ratio of barium to strontium salts in groundwater was different at different levels.

Many investigators that studied the origin of barite note that, whatever the type of barite deposit, the barite was most probably derived from mixing of juvenile (rising) water carrying from depths barium chlorides and other soluble barium salts with vadose (descending) water containing sulphates. We have no data, however, on the barium carried by deep waters. In addition, no compounds of this element are present low in the sulphur ores. Hence the conclusion that the barite in the sulphur ores is due to dissolution of the barite disseminated in limestone by hydrocarbonate water. The barium migrated as bicarbonate. Getting into an environment with a highly elevated content of the sulphate ion, the bicarbonate precipitated at once



Strontium-bearing barite

as barite. The appearance of barite, in which sulphur has the highest valence, in the sediment indicates a much greater oxygen potential in solutions at the time of origin of the mineral.

The presence of several barite generations was caused by changes in the environment. When the solution was supersaturated but slightly, relatively scarce crystallization centres appeared, which resulted in precipitation of large calcite crystals. When the solution was supersaturated strongly, fine-grained barite was formed. The first barite generations contained less strontium (see Table). The zoned crystals found indicate pulses of input of mineralizers and breaks in mineral deposition. At the closing stages, the solutions were very viscous, lead-

Chemical Composition of Barite, wt%

Component	Colourless crystals, generation I	Brown crystals, generation II	Zoned milk-white crystals, generation III	Strontium-bearing barite, generation IV
BaO	64.21	62.27	63.92	59.98
SrO	0.25	0.48	0.62	1.54
CaO	0.05	0.38	0.38	0.74
MgO	0.07	0.05	0.17	0.94
SO_3	34.29	35.50	33.08	33.40
SiO_2	0.74	1.63	0.68	1.90
H_2O	0.12	0.08	0.38	0.14
Total	99.73	100.39	99.23	98.64

ing to the appearance of skeletal crystals. While the edges and apices were wholly surrounded by the feeder, this was not the case at the centre of the faces. Because of this, the faces gradually left behind the apices and edges, and the crystal was becoming skeletal.

Resistance of Stone to Weather

Having originated under certain conditions, stones and their constituent minerals may live rather long until these conditions change radically. Stability is the most important property of all minerals. It depends on the character of interaction between molecules and between atoms. The destruction of a mineral leads to destruction of chemical bonds in it; its physicochemical and optical properties change. This process leads at the same time to the origin of a new mineral, secondary as to be previous one. Fortunately, the environment changes slowly and hence minerals have a long life which often lasts tens and hundreds of millions of years.

Stones in constructions also live differently: some easily withstand atmospheric agents, others are destroyed together with the construction, and still others adjust to changing conditions. Each stone and mineral has thus its own life, peculiar and remarkable. Perhaps it can be compared to the life of plants.

A similarity lies in the fact that groundwater that often contains soluble salts rises up the walls of any stone building. The capillary rise of groundwater moisture is stronger, the drier and hotter the climate. For instance, groundwater, which is usually salty here, rises in Soviet Central Asia as high as 3 m. In Kazakhstan, groundwater penetrates into inner premises leaving behind white efflorescence on the walls of flats. In Moscow, salts rise as high as 1 m, and this process intensifies greatly when pavements are sprinkled with salt.

Much has been written in recent years about the "wounds" of Parthenon—a masterpiece of Greek art built in honour of the goddes Athena, patroness of Athens. Parthenon has been amazing everyone with its white marble columns and bright paintings since ancient times. One of the "wounds" is inflicted by tourists. As many as six thousand people visit the temple each day (4.5 million people in 1977), and they wear down steps and marble plates of the floor. The granite steps of the British Museum, London, are worn down more slowly, though throngs of visitors have been walking on them for the past 300 years.

Wearing down has been proved to be not the main danger for the stone. The main foe is water containing two acids—sulphuric and nitric. A very strong influence is also exerted on the stone by atmospheric contamination, temperature fluctuation, humidity of the air and microorganisms. Like some metals, the stone expands on heating and contracts on cooling. As a result, it becomes no more lovely coloured and transparent, and its hardness and density are lowered. The stone also loses other useful properties. The clay contaminant, predisposed to weathering, is especially undesirable in decorative stone. Limestone plates become turbid in the air and lose their attractive appearance; fine cracks cut along clay streaks. Rain water dissolves about 1 mm of marble in a century. Snow acts stronger than rain, because it absorbs more chemically active compounds from the air.

Changes in rocks induced by temperature fluctuation consists in crystal destruction on cleavage planes and in microjointing. The main factor of frost weathering is a change in the physical state of water. Hygroscopic water attracted by many minerals under the effect of surface energy penetrates into minute cracks and opens them up, thus easing the penetration of capillary and free water into them. On freezing, this water can push the fracture walls apart perceptibly. This is because when water freezes it acts on initial fracture walls with a pressure as high as 2 100 kg/cm^2. But in the opinion of the geologist A. Viktorov, frost weathering of the stone whose cavities are occupied by water progresses along a different path. The ice formed freezes the outer openings of capillaries and fractures and starts to press upon yet unfrozen water inside these capillaries. The finer the capillary, the greater the pressure and the longer the water inside the capillary remains liquid. It is this water, rather than ice, that tears apart the walls of capillaries.

A characteristic process affecting calcite, marble or limestone at the Earth's surface is their calcification and related heaving. This is caused by calcite being converted to gypsum, hydrous calcium sulphate.

Marble gypsification results from the effect of sulphuric acid on calcium carbonate; this acid forms in large cities according to the following reaction with the participation of refuses of industrial plants and combustion gases released by cars:

$$CaCO_3 + H_2O + H_2SO_4 = CaSO_4 \cdot 2H_2O + CO_2$$

The reaction is based on replacement of the weak anion CO_3^{2-} by the strong anion SO_4^{2-} in an acid environment ($pH = 4.3$ and lower) with carbon dioxide liberation.

This is how white-marble Parthenon is being destroyed. In bad weather, white marble, which was excavated by slaves in the quarries on Mount Pentelicus, is cut by cracks into which water penetrates. It expands on freezing and breaks up marble blocks. The pressure of a water drop frozen at night can be compared to that of a 1.5-tonne truck per 1 cm^2.

The exhaust gases from the plants in the vicinity of Athens, and rain water calcify marble severely. It loses its intrinsic colour and lustre, and becomes covered with a thin crust and light-grey drips. It heaves at places because of expansion due to calcite-to-gypsum transition. The resulting gypsum makes pressure on fracture walls and push them apart. Its crystallization in the cracks acts on marble in the same way as freezing water. The pressure made by growing gypsum is occasionally so great that the mineral is squeezed out as small mounds and swells onto the surface of the object.

The contaminated atmosphere is a global-scale cause of stone destruction. A demonstrative example is offered by Venetia—a pearl of world culture. Goethe writes that Venetia is a dream made of air, water, earth and sky. An annual amount of 15 thousand tonnes of concentrated sulphuric acid is thrown into the air in only one of the Venetian suburbs together with wastes of industrial plants and combustion gases, and this acid then drops onto the earth together with rainwater and fog. The most prominent constructions in the city (basilica Saint Mark and the Palace of the Doges) are built of marble. They were built as early as the 9th century and since then are gradually being destroyed. Each year, Venetia loses 6% of marble article, 5% of frescoes and 3% of paintings.

Deteriorating are the marble monuments of Leningrad (Isaak Cathedral, which is faced with pink marble from Karelia), Moscow (Pushkin Art Museum, with its beautiful columns of white Uralian marble) and other cities. In the white-stone buildings of Moscow, gypsum composes up to 7% of the surface zone and less than 1% deeper in the wall. But once the facing is protected from bad weather, the same marble or limestone will be kept polished not one year, and inside the building the soft stone will become quite long lived.

The stony facing also deteriorates in appearance owing to white efflorescence. Their precipitation is observed nearly everywhere.

All this confirms a great role played by moisture in mechanical destruction of marble. But moisture not only destroys the stone; it is a favourable medium for microorganisms. Colonies of bacteria reproducing themselves in damp ease the generation of the so-called stony lichen. Its green blooms and patches are found on the north side and, in general, in the shadow of many "wet" marble monuments. They not only make the stone looking mossy but also destroy it. The geochemical role of microorganisms consists in absorption of sulphur oxides from the environment and promotion of marble transformation into gypsum. Wetness and associated bacterial activity participate in the destruction of Borobudur, the largest and most ancient (about 800 A.D.) beautiful monument in the south of Yava Island.

The capital of the ancient Khmer state, the outstanding architectural memorial founded as early as the 9th century, is also being destroyed very rapidly. The destruction is due to microorganisms abundant in a humid climate. The marble of the Palace of Doges in Venetia suffers from the same "disease".

How can the life of the stone be prolonged? To answer the question, a laboratory was created in Paris; here, in a special chamber, comprehensive studies were made of changes in building stone under the action of a simulated environment. It has been found that the presence of the stone in this environment for two years is the same as its presence in the open air for a quarter of a century.

What are the recommendations offered by scientists to prevent stone destruction under superficial conditions? One of them is treating the stone with zinc, aluminium and calcium soaps of naphthenic acids. Unlike common sodium soap, these are not wettable and cannot dissolve in water. A thin film of metallic soap mantles pore mouths while the rest of the pore remains unfilled. This is quite enough for the stone to be sealed off.

Another recommendation is that a polymer film that adsorbs any contamination is applied to the surface of a sculpture. On drying up, the film is rubbed away with a soft cloth leaving behind a pure surface. Depending on its porosity and degree of preservation, each material is treated with a specifically designed film-forming composition.

To prevent it from destruction, it is recommended that the stone be penetrated with fluosilicates. In reacting with the minerals, these salts produce calcium fluoride, silicon hydrate and other insoluble compounds. As a result, the superficial layer of the stone becomes more compact and less hygroscopic. Stone painting and whitewashing are also practised.

To fight effectively against efflorescence, their mineral compositions should first be known. Until recently, however, this subject was dealt with only slightly in specialized literature. The main method to devoid of this evil is still its mechanical removal by sand from sandblasters or by hot steam, which is rather labour consuming. Greek scientists have recently successfully used lasers to remove sulphates from the surface of marble sculptures.

One of the techniques of saving ancient monuments implies their restoration with the help of the same materials and procedures that were used in initial treatment of the stone. Archaeologists just practise it on Yava Island. In the opinion of many researchers, the gradually destroyed architectural monuments of Venetia can be saved by replacing the cut stones that make up the walls of cathedrals and palaces. Suitable stone resistant to sea water has been found in Jugoslavia.

The detrimental effect of the contaminated atmosphere can be observed on the famous Cologne Cathedral. The stones of the cathedral were appreciably touched by erosion already early in the 20th century. Hence it was proposed as early as 1903 that the whole cathedral be placed under a glass cover. It was markedly damaged during World War II but was restored soon to its original appearance. But destructive erosion has not spared its walls this time also. Then the glass cover project was considered again, but it should not be spherical in this case but coinciding with the shape of the cathedral. It is proposed that the stone be purified beforehand from dirt, the pores filled with silicon and its surface coated with a waterproof acryl film.

The destructive action of microorganisms can be stopped by injecting penicillin into the superficial layer of the stone. At present, builders tend to abstain from using marble, especially in large industrial hubs.

The World of Crystals

Man gave attention to the regularity of forms of crystals but believed that they are extremely scarce and are a peculiar play of Nature. They thought in ancient times and the Middle Ages that quartz crystals are the same as ice crystals, the only difference being that ice freezes under our very eyes and quartz at a very low temperature. The very word crystal is from Greek *krystallos*, which means ice.

The crystalline state is one of the fundamental properties of matter. Crystals constitute 95% of the Earth's crust. The bulk of them have passed through time, adjusted to the environment and become useful to man. Crystals are around us. We extract them from the Earth's interior to study in laboratories, treat at factories, and create articles. We walk over crystals and use them widely in our everyday life. Salt and sugar, ice and snow, clay and sand, and hundreds of other substances—

all of them are crystals. The results of modern crystal studies are of utmost importance for other sciences, in particular for biology. Natural crystals, for instance those of clay minerals, may have served as matrices on which molecules had been formed to give rise to life on our planet.

The science that is concerned with crystals, their structure, shape, and physical and chemical properties, emerged within the framework of mineralogy and has long been part of it. All the basic laws of crystallography were discovered while studying minerals. Then crystals became the object of investigations by physicists, chemists, mathematicians and even biologists. Crystallography is a substantive science; it adjoins many fields of knowledge, enriching them in its theoretical and experimental methods and borrowing their techniques for further and deeper crystal investigation. A mineral in the form of a crystal is in the most perfect state, and this makes us feel a delight.

However, crystallography has not broken away from mineralogy. Moreover, the teaching of natural crystals has risen to a higher theoretical level. Practical demands, discoveries and exploitation of extremely valuable crystal deposits, and advances in single crystal growth techniques have revived mineralogical crystallography, which had been in the shadow until then.

It is interesting to trace the origin and development of crystallographic teaching with reference to natural objects. Crystals are regular in outer appearance because they are symmetrical. “Crystals are radiant with symmetry”, as the outstanding Russian crystallographer E.S. Fedorov underlined. Symmetry is from a Greek word meaning uniformity, commensurability, due proportion and harmony. Symmetry is a property of objects or of their parts to be equal to each other in some or other sense. Formulation of the notion of symmetry has a long history.

A feeling of rhythm and symmetry, proportionality of volumes in constructing art compositions are fully present in palaeolithic “Venuses”, in paintings of animals on bones and stones, in rod heads and in cliff drawings. They appeared at the very beginning of fine arts. The extremely simple ornament of palaeolithic art is, as a rule, geometrized. First, this was a row of straight and wavy lines, spirals and dots, then concentric rings, triangles and other figures and then images of men, animals, and elements of plants often perceived as a geometric pattern.

Naturalists and thinkers in ancient times expressed symmetry with the help of geometric plots and numbers. The symmetry of surrounding objects overwhelmed ancient man by its perfection. Striking regular outlines of crystals caused a superstitious fear and worship. Thus, symmetrical figures (ring and sphere) in the Pythagorean teaching were not only embodyments of perfection but also exerted a mystic effect. The ancient Greek scientist

Plato (428 or 427-348 or 347 B.C.) postulated that the world consists of regular polyhedra having an ideal symmetry. He attached special importance to these bodies, considering them to be embodiments of four elements: fire, earth, air and water. According to Plato, all physical bodies are mathematical entities composed of triangles regulated by demiurge (creative spirit). The problems of symmetry and harmony of material objects were attacked by many philosophers and naturalists: da Vinci, Leibnitz, Descartes, Spencer, Hegel, etc.

In everyday life, man constantly come across symmetry, finds it intuitively, feeling an esthetic delight. Moreover, on revealing symmetry in nature, that is in the structure of bodies of animals and plants, man saw that the symmetrical thing was handy and easy to manufacture. Architecture and fine arts, wonderful creations of the human race, cannot even be imagined without symmetry, that is symmetry of geometrical figures. However, the notion of symmetry is taken to be much wider; it is dealt with in various fields of science and art: in music, mathematics, and poetry. In recent years, great advances have been made in the French physicist P. Curie's (1859-1906) theory of the symmetry of physical phenomena.

The Dutch N. Steno (1638-1686) came to the conclusion while examining quartz and hematite that angles between particular faces remain constant though crystals of one mineral are different in shape. The French investigator Romé de L'Isle (1736-1790) extended this property in 100 years to include all crystalline substances. It was later called the Law of Constancy of Interfacial Angles, the fundamental law of crystallography.

N. Steno not only discovered the Law of Constancy of Interfacial Angles but was also first to reveal the mechanism secret of crystal growth. He wrote that a crystal grows not from inside, like plants, but by superposition of minute particles supplied from the outside by some liquid on the outer planes of the crystal... . The crystal grows until new crystalline matter is attached to the outer planes of the already formed crystal.

Proceeding from the Law of Simple Rational Intercepts, the German mineralogist J. Hessel (1796-1872) geometrically proved in 1830 that only 32 crystal classes are possible in nature. No attention, however, has been given to this work. Though being unaware of Hessel's publications, the Russian scientist A.V. Gadolin (1828-1892) confirmed in 1867 the existence of 32 kinds of symmetry for crystalline polyhedra.

A symmetric polyhedral shape is inherent in many crystals. Most of them look like regular polyhedra with planar faces. Thus rock salt crystals are cubes and the gemstone diamond more often than not occurs in nature as octahedra.

The internal structure of crystals also obeys the laws of symmetry. With the help of invisible rays discovered by W. Roentgen (1845-

1923) in 1895 and called X-rays, atoms were proved to exist inside the crystalline body and their spatial arrangement was determined. It was found that all crystals consist of atoms, ions and molecules arranged in a strict, mathematical order. One can also judge upon the internal, atomic structure of a crystal on the basis of its shape, which reflects the character of packing of atoms. For instance, sodium chloride atoms in common salt are packed in cubes; hence, crystals of this mineral are, accordingly, cubic.

The English chemist and physicist W.H. Wollaston (1766-1828) put forward in 1813 an idea of sphericity of molecules, which were depicted, for the limiting case, as mathematical points. Their regular disposition in space gave rise to the notion of crystal lattice symmetry. This is a kind of mathematical abstraction, a mathematical image based on the structure of material. Straight lines along which particles in the lattice are arranged are called rows, and planes covered with particles, planar nets. To lattice points, rows and planar nets correspond apices, edges and faces of the crystal. The best developed and most common faces on the crystal coincide with the planar nets having the greatest number of particles on them.

Although each atom in the crystal occupies its own place at a certain point of the lattice, many processes are known which disturb this pattern. One of such processes is the migration of atoms between lattice points.

The crystal lattice of a mineral is composed of unit cells continually built up until the mineralizer contains appropriate material and is under favourable thermodynamic conditions. Giant crystals grow in the most favourable environment, otherwise the crystal loses its coherence and grows no more.

The internal structure of a crystal is much richer in symmetry elements than its external form. In 1890, E.S. Fedorov derived all possible (230) space groups of symmetry elements. The laws of arrangement of atoms form the foundation of structural crystallography.

Both the external and internal arrangement of symmetry elements in a crystal is due to its structure and the structure of the environment. Crystal structure plays a greater role if the bonds in it are stronger than those in the environment. When these are similar, the latter become prevalent.

The structure of crystal lattice determines the remarkable properties of crystals. One of them is anisotropy—nonuniformity of properties of crystals in different directions. For instance, a mica sheet splits readily in one direction and extremely hardly in the other. Anisotropy is a distinctive feature of a crystalline material as compared with an amorphous substance. An important characteristic of most crystals is cleavage, in other words, capability of splitting in certain directions.

Thus if a rock salt crystal is hit with hammer, it will split into smaller cubes which, in turn, can be broken into even smaller ones.

Cleavage varies from crystal to crystal. This property should be taken into account in faceting precious and semiprecious stones. Crystals can divide light into rays, turn electric fluctuations into acoustic ones, stabilize high-frequency electric oscillations (radiowaves), converge alternating into direct current and ultrasonic signals into electric oscillations, and so on. The useful properties of crystals are practically limitless.

In natural crystals, the strict periodicity of atoms is disturbed to some or other degree. These are defects of crystal lattice. Such defects are vacancies, interpoint atoms, contaminants, dislocations, microfractures and so on. The defects strongly affect the mechanical, thermal, magnetic, optical, chemical and other properties of crystals. Crystalline substances containing various defects are used widely in manufacturing metallic constructions, semiconductor devices, lasers and masers.

The notion of symmetry has been known since long ago. Bodies that are composed of identical parts are symmetrical. These parts can coincide. Symmetrical are a butterfly (it has identical left and right parts of its body), a snow-flake, a leaf, and so on. If the butterfly folds its wings, these will match each other. Hence we say that the halves of the butterfly are mirror-reflected, or the butterfly has a plane of symmetry. Snow-flakes—crystals of frozen water—have even six symmetry planes. Therefore, these planes divide the crystal into several equal parts each of which is something like a mirror reflection of another one.

The next element of symmetry inherent in crystalline bodies is the centre of symmetry. This is a point inside the crystal which has the following property: on any straight line through it the relevant points of the crystal lie at equal distances from it.

The axis of symmetry is a straight line about which the crystal can rotate in such a way that it will coincide with its previous position twice or more times. Depending on the rotation angle, second-, third-, fourth- and sixth-fold symmetry axes are distinguished.

Any crystal is divided into simple forms. The notion of a simple form is basic for the teaching of crystal forms. A simple form is a combination of faces mutually related through elements of symmetry. All the faces of one form on a perfect crystal should be quite equal in size (they are derived from symmetry elements). There are 47 simple crystal forms. But far from all of them play an equal part in bounding of crystals. Moreover, these forms produce various combinations, rather than occur separately.

Interfacial angles and areas of faces are major metrological characteristics of a crystal concerning both the relative development of the faces of one simple form and the ratio of areas of faces on different simple forms. The appearance of a simple form on a crystal and the ratio of face areas are due to the environment of mineral formation.

Perfect crystals are rare creations of Nature, the result of its long-lasting and painstaking work in the Earth's interior. It could be imagined that the equal faces of these crystals would move equidistantly away from the centre. It is in this case that ideal crystals could arise. In nature, however, even the most perfect crystals are never ideal; a close examination would invariably reveal some deviations from an ideal symmetry. It has been found that the causes are not only the crystal and environment but also the factor of time. V.I. Vernadskii wrote about it as early as the 1930s; he underlined that deviations from the ideal symmetry of crystals are due to the nonsymmetry, nonreversibility of time.

To better understand crystallographic terms, let us imagine a centrally lying coordinate system whose main directions would be parallel to the principal edges, axes and symmetry planes of the crystal. Place the crystal in such a way that the highest-order symmetry z-axis was vertical, x-axis was directed towards the observer and y-axis, to the right. This is a three-axis coordinate system. In the four axis coordinate system, the x-, u- and y-axes are in the horizontal plane at 120° relatively to one another, while the z-axis is normal to them. By this indication, all crystals can be classified into seven systems: isometric, tetragonal, orthorhombic, monoclinic, triclinic, trigonal and hexagonal. Each system has its own symmetry elements and associated external form of the relevant crystals.

The coordinate system can be used to establish the angular position of crystal faces. Each face is designated by a symbol—parenthesized indices. These are sinus of angles between the crystal face and coordinate axes. Indices are small whole numbers. There are three such numbers in the three-axis coordinate system and four in the four-axis one. A larger index depicts the face that has a greater angle with the axis. If the face is parallel to some axis, its index for this axis is equal to zero. Thus, symbol (100) implies that the face intersects the x-axis, which is directed to the observer, and is parallel to the two remaining y- and z-axes; face (110) is parallel to the z-axis and intersects the x- and y-axes. A similar picture exists also in the four-axis coordinate system; in particular, the trigonal system, in which calcite crystallizes, has four indices, rather than three. A crystal can consist of one or more simple forms. Their symbols are braced indices of the face that is nearest to the observer in the frontal upper (positive) part of the coordinate system.

The case of calcite consists in an extremely great number of simple forms (over 700) on its crystals. In this respect, calcite holds the record among other minerals. However, the combination of faces of individual crystals is commonly very poor. Many crystals occur only in one form (rhombohedron, scalenohedron) or in a prism bounded by the faces of a rhombohedron and pinacoid. These four forms are principal ones for calcite crystals.

Their prevalence determines the habit (rhombohedral, scalenohedral, pinacoidal) and appearance (elongate, isometric, flattened).

Most of the known crystals are tens, more often hundreds of millions of years old, whereas the formation of their synthetic analogues is nearly instantaneous from the geological viewpoint. Giant crystals of quartz, equal in height to a man, of feldspar, equal to a large room in size, mica sheets as big as a modern shop window vividly demonstrate the size limits of the crystalline state. These crystals were derived from complex geochemical processes in the Earth's interior during millions of years.

Younger crystals, whose age varies between millions and thousands of years, were generated closer to the Earth's surface. Tens of years were spent to observe the growth of several stalactites in one of the caves of the Monaco Kingdom. It has been found that sinter grows at a rate of 0.4 mm/year, that is elongated by merely 4 cm in one hundred years. A man who broke off a one-metre stalactite destroyed what the Nature has created during two and a half thousand years.

Slow is the growth of carbonates in modern sediments. The scientists of the University of California observed the growth of dolomite crystals in today's sediments of Lake Dean Spring (California) by employing the radiocarbon method. According to their estimates, the crystals grow at an average rate of 0.05-0.09 μm in one thousand years.

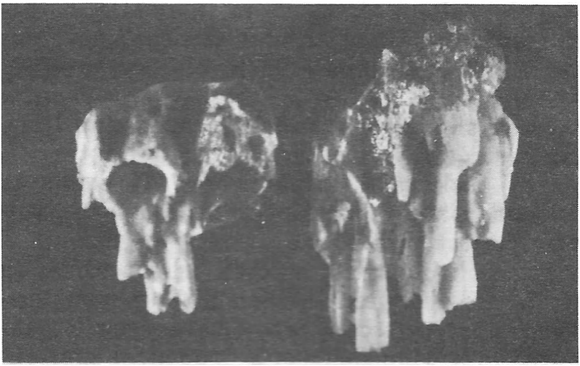
The Mystery of Onyx Marble

Calcite

Calcite is one of the widespread minerals in sedimentary rocks and the principal mineral of sulphur ores. Scientists have long been intrigued by the mystery of onyx marble—calcite the colour of which is in gentle, pastel tinges; in combination with transparency, this has made it famous as a lovely semiprecious stone.

In sulphur deposits, calcite makes up limestone strata, and occurs as an admixture in clayey rocks and sulphur ores. It exists in pelitomorphic, fine-grained and coarse-crystalline generations.

The pelitomorphic calcite, which varies in grain size between 0.005 and 0.01 mm, can be primary or secondary. The former is generated in a wide range of geochemical environments. It forms the substrate on which complex transformation of organic molecules takes place. This calcite constitutes dolomitized and pelitomorphic limestones wholly unrelated to native sulphur. In the dolomitized limestones, which are sulphur-enclosing rocks in some deposits, the pelitomorphic calcite is associated with dolomite grains and clay. The primary pelitomorphic limestones are more extensive than the secondary, which lie lower in the section. In the Rozdol'skoe deposit, they are massive, thick-platy, bedded, frequently alternating with clay and grading into it. That the limestone is of sedimentary origin is confirmed by fossil evidence. In the Podgornenskoe deposit, the pelitomorphic limestone occurs in sandstone above the sulphur ores. The same limestone in the Gaurdakskoe deposit predominates in the Gissarskaya and Gaurdakskaya formations. The pelitomorphic calcite is also part of marl widespread in the upper strata of the Vodinskoe and Rozdol'skoe deposits. The groundmass of the marl is composed of 0.005-mm calcite grains, and clay particles constitute 50 to 65% of the marl.



Stalactite-like calcites

A mineralogical mystery is secondary pelitomorphic calcite. It is the same in some properties as the primary pelitomorphic calcite. This is a chemogenic carbonate derived from complex chemical processes, rather than from the activity of living organisms. In a number of regions, in particular in the Ciscarpathians, commercial reserves of native sulphur are associated with the chemogenic calcite.

The pelitomorphic calcite is made up of irregular grains ranging in size from 0.005 to 0.01 mm. It contains perceptible amounts of clay concentrating on the periphery of the grains and in-between, and is associated also with quartz and glauconite grains, and with organic matter. Its characteristic feature is that it is inequigranular, which is seen even in limited areas. Thin sections frequently show wedge-like areas of pelitomorphic calcite clearly distinguished by small sizes of grains against the background of coarser carbonate.

The pelitomorphic calcite is closely associated with fine-grained sulphur. The finer the grains of one mineral, the finer are those of the other. An increase in the size of grains of pelitomorphic calcite results in its becoming more idiomorphic. The outlines of the mineral become more distinct, and the amount of impurities in it decreases. Some grains of the pelitomorphic calcite have branches; as a result, these grains interlock with sulphur grains. An impression can be made that sulphur and calcite intergrow. The intensity of such intergrowth depends on the size of sulphur and calcite grains. The intergrowth is closest when the two minerals are finest and approximately equal in size. Under the microscope, such a sulphur-calcite aggregate is coloured grey, and this colouration remains the same in crossed nicols on rotating the microscope's stage.

The pelitomorphic calcite composes the bulk of ores in the Ciscarpathian sulphur basin. These ores do not lie at a definite level in the sulphur body. In the composite section, however, it is seen that the ores that are composed of pelitomorphic calcite constitute the lower part of sulphur bodies, whereas their upper part consists of coarser-grained limestone.

The fine-grained (grains ranging from 0.1 to 1 mm across) calcite was mainly derived from recrystallization of the pelitomorphic variety of this mineral. In a broader sense of the term, recrystallization is any morphological change in an individual with no changes in its chemical composition (increase or decrease of grain size, habit changes). We use this term in a geological-petrographical sense, taking it to mean solely processes leading to grain enlargement. when some individuals grow at the expense of others without a mass exchange between the crystalline aggregate and the environment.

There have been distinguished nestle-like, banded, lens-like and massive recrystallization types. With the last. the carbonate rock changes its appearance nearly completely, its primary fabrics becoming blurred. Recrystallization thus produces rocks that are quite non-uniform in fabrics. and this eases rock disturbance by tectonic processes with the formation in them of various cavities along cracks and interpore channels. More seldom is fine-grained calcite derived from gypsum replacement. It then commonly contains host rock relics. The fine-grained calcite from the Vodinskoe sulphur deposit was derived from pelitomorphic dolomitized limestone. The areas of newly formed calcite have irregular outlines, with numerous "tongues" into the dolomitized limestone. The fine-grained calcite is widespread in thin veinlets constituting a reticulate pattern in the pelitomorphic limestone. The calcite is older where it is associated with granular sulphur. The Vodinskoe deposit displays spherulites made up of small columnar crystals of calcite. It is possible that the presence of mechanical impurities and some chemical elements in the mineral-forming solution is made for the crystallization of the spherulite-forming system.

The coarse-crystalline calcite (grain size more than 1 mm) is the result of recrystallization of the pelitomorphic and fine-grained varieties and of direct precipitation from solution. Like other crystalline bodies laid down in hollow cavities, calcite has a remarkable property of spontaneously taking the form of a crystalline polyhedron.

The calcite from sulphur deposits is distinguished by the restriction of its crystals of a certain habit (rhombohedral, scalenohedral, prismatic) to the different parts of the orebody and by the presence of needle-like scalenohedral individuals, peculiar phantom crystals and their intergrowths in which the inner crystal (phantom) differs in appearance and colour from its enclosing polyhedron.

Two calcite varieties are observed in the sulphur deposits of the Ciscarpathians. One of them, less common, occurs as rhombohedral crystals with the habitual form $\{02\bar{2}1\}$, coloured in various tinges of yellow. More widespread are younger colourless scalenohedral calcites. Both varieties are present as single individuals, various aggregates (vugs, brushes) and masses. The calcites differ not only in habit but also in location in sulphur ores. In the upper part of sulphurized limestone, the calcite occurs together with barite and has a rhombohedral habit. Towards the base of the orebody, the habit is becoming rhombohedral and scalenohedral. In areas of celestite mineralization, the calcite is nearly always found as scalenohedra with the habit form $\{21\bar{3}1\}$, other scalenohedra ($\{7\cdot7\cdot\overline{14}\cdot3,\ 62\bar{8}1\}$) being subordinate. The rhombohedral crystals are up to 0.5 cm along threefold axis, and scalenohedral crystals, 1 cm. Some individual crystals are zoned owing to clay inclusions on the planes of the fundamental rhombohedron $\{10\bar{1}1\}$. Splitted individuals have been found among the scalenohedral crystals.

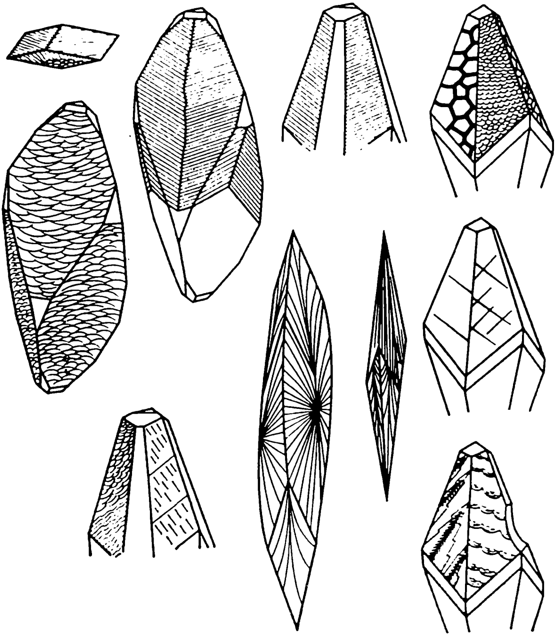
Calcite aggregates resembling stalactites in external form remain puzzling. They hang from the ceiling of a cavity or the inclined wall of a fissure, being as long as several centimetres. The aggregates have a rough surface, because they are composed of small rhombohedral calcite crystals whose threefold axes radiate from the growth centre. An interesting feature is that some of these aggregates are penetrated by a thin pipe open at one end; a small sulphur crystal attached to the base of the aggregate may occur inside this pipe. More seldom are parallel and columnar calcite aggregates up to 11.5 cm long. They grew towards each other on the substrate of granular calcite or on parallel-columnar gypsum crystals. The calcite from the Vodinskoe deposit occurs as well-defined crystals that are isolated, line vugs and form thin crusts. They constitute segments of recrystallized limestone containing little or no sulphur. The calcite is associated there with liquid or solid bitumen, which generally makes up the central part of a calcite concretion. With rare exceptions, the crystals are scalenohedral with the habit faces $\{21\bar{3}1\}$, $\{8 \cdot 16 \cdot \overline{24} \cdot 5\}$ and the subordinate planes of the rhombohedra $\{10\bar{1}1\}$, $\{13 \cdot 0 \cdot \overline{13} \cdot 1\}$, $\{40\bar{4}1\}$ and a prism $\{10\bar{1}0\}$.

The calcite from Vodinskoe forms "barley grain-shaped" intergrowths built up of curved individuals, and also two-coloured phantom-crystals. The inner crystal is brown bituminous calcite while its enclosing scalenohedron is colourless and transparent. The course of growth of such crystals is still known incompletely; the mineral-forming solutions had an intermittent character.

The calcite crystals are elongated, scalenohedral and sharply rhombohedral; they are as large as 1 cm along the threefold axis.

Predominating are rhombohedra with the habitual plane $\{03\bar{3}1\}$ and a curved scalenohedron whose habit cannot be determined. Needle-like scalenohedral crystals with $\{26\bar{8}1\}$ are quite extensive.

Calcite crystals and their intergrowths are scarce in ores from the Gaurdakskoe deposit. The crystals are scalenohedral, with the habitual facies $\{14{\cdot}2{\cdot}1\bar{6}{\cdot}3\}$, $\{6{\cdot}8{\cdot}1\bar{4}{\cdot}3\}$ and



Etching figures on calcite crystals

$\{9\cdot17\cdot\overline{26}\cdot2\}$. Rhombohedra $\{02\bar{2}1\}$, $\{40\bar{4}1\}$ and $\{10\bar{1}1\}$, and a prism $\{11\bar{2}0\}$ are of minor importance. The calcite from the Changyrtashskoe deposit has but one simple form, a rhombohedron $\{02\bar{2}1\}$. Rhombohedra with the habitual face $\{08\bar{8}1\}$ predominate among the calcites from the Mishrakskoe deposit. Only one form, $\{6\cdot8\cdot\overline{14}\cdot3\}$, has been identified in the scalenohedra. The crystals are rhombohedral at shallow depths and scalenohedral at large depths.

The calcite crystals from the Podgornenskoe deposit are rhombohedral, rhombohedral-prismatic and scalenohedral, the first predominating. Changes in the calcite habit with depth have been traced. The calcite from the Zhilyanskoe sulphur occurrence discovered at the Earth's surface is rhombohedral and prismatic, bounded by the faces of a rhombohedron $\{02\bar{2}1\}$ and a prism $\{10\bar{1}0\}$. At a depth of 140 m, the habit becomes rhombohedral with the prevalence of a form $\{40\bar{4}1\}$. The orebody growing downwards, blunt rhombohedra $\{01\bar{1}2\}$ have been found at 237 m of depth. At a depth of 259 m, crystals become scalenohedral, with the best developed face $\{10\cdot5\cdot\overline{15}\cdot4\}$, at the contact with gypsum-anhydrite.

The calcite crystals are rarely smooth and bright; they are generally covered with various figures related to their growth or dissolution. The growth figures are straight, gently curved, zigzag and occasionally closed. Parallel straight lines look like striations, semicircular ones, like fish scale or carefully laid tile; and closed growth layers, like small triangles. The curved individuals are covered with delicate radial-fibrous striations. Dissolution figures on the crystals are seen as straight, striation-like or gently curved notches. Some of them are filled with bitumen, which proves vigorous effect of bitumen-bearing solutions on the mineral. If dissolution begins with edges, the crystals acquire a characteristic curved shape.

Many publications deal with crystallization of calcite; the morphology of its crystals is known to depend greatly on the mode of its origin. It is generally accepted that the evolution of calcite habits is due to a crystallization temperature drop or a gradual decrease of mineralizer supersaturation.

The calcite from sulphur deposits appear at low temperatures. Hence the influence of temperature on crystal habit is ruled out. The main factor that affects calcite forms with passing time is, according to the mineralogist N. Evzikova, the changes in the degree of solution supersaturation. She has found that the faces of crystals tend to be less and less compact in the course of their crystallization from one solution batch. Her sequence of simple calcite forms is as follows: $\{0001\} + \{10\bar{1}1\} \rightarrow \{10\bar{1}1\} \rightarrow \{01\bar{1}2\} \rightarrow \{10\bar{1}2\} + \{10\bar{1}0\} \rightarrow \{10\bar{1}0\}$ or, accordingly, lamellar individuals → rhombohedra → prisms → scalenohedra → sharply terminated rhombohedra. This sequence is not always realized in nature. Evzikova later referred to the compactness of faces, not as that of planar nets but as that of the unit layer of the face—a layer of minimum thickness that can form on a crystal face and contain the minimum number of all the planar nets characteristic of the face. The mineralogist R. Aliev's calculations on the compactness of unit layers made on this principle yields the following values: 6.78 for $\{0\bar{2}21\}$; 5.35 for $\{10\bar{1}1\}$; 5 for $\{0001\}$; 3.36 for $\{01\bar{1}2\}$; 2.69 for $\{21\bar{3}1\}$ and 2.55 for $\{10\bar{1}0\}$. Let us see how this series is realized in the sequence of calcite habits at the Podgornenskoe sulphur deposit. We'll attempt at correlating the habit with the isotopic composition of carbon from the calcite.

At present the isotopic composition of carbon, sulphur and other elements is widely invoked to solve a number of geological problems. The isotopes of one and the same chemical element differ in atomic weight but are nearly the same in their chemical and physical properties. Because of subtle distinctions in their atomic weights due to a varied number of neutrons in their nucleus, the isotopes of a certain chemical element behave differently in one and the same process. In certain physicochemical processes, insignificant differences in properties lead to isotope partition the value of which is measured on a mass spectrometer. This value depends on particular natural conditions. Therefore, if we know the principal processes that partition the isotopes of an element and can determine its isotopic ratio in this or that sample, we can judge upon the physicochemical environment of mineral formation.

Carbon has two isotopes, ^{12}C and ^{13}C, that provide the most valuable information. The average for $^{12}C/^{13}C$ is taken to be 89.3. The isotopic composition of carbon can also be characterized by $\delta^{13}C$—a difference in per cent between the contents of ^{13}C in the particular and the reference sample.

My first attempt to assess the effect of some crystallization factors on the isotopic composition of carbon in the solution from which calcite precipitated was made in 1977. I assumed that the isotopic composition of the solution cannot control the crystal shape because the difference in the surface energies of crystal forms and that in the free energies of isotope forms are values of different orders.

The samples to be studied were taken in an area where the sulphur ores occur in the upper part of sulphate rocks. The orebody grew here downwards. It was natural to suggest that the habits of calcite could have given way to one another in the same direction. In the Zhilyanskoe sulphur occurrence the calcites from the outcrops of sulphurated limestones are oldest and that taken from some 260 m of depth, youngest.

The calcite habit apparently evolved from rhombohedral-prismatic to rhombohedral and scalenohedral habit against the background of the light isotope ^{12}C increasing in amount in the mineral-forming solution has, hence, in the calcite. In this process, $\{02\bar{2}1\} + \{10\bar{1}0\} \rightarrow \{40\bar{4}1\} \rightarrow \{01\bar{1}2\} \rightarrow \{16 \cdot 8 \cdot \overline{24} \cdot 5\}$.

The correlation of this series with that obtained by R. Aliev shows that these are akin. Both begin with $\{02\bar{2}1\}$ and include a rhombohedron $\{01\bar{1}2\}$, which gives way to a scalenohedron. The distinction lies in that the calculated series ends with a prism $\{10\bar{1}0\}$, while the obtained one, with a scalenohedron $\{16 \cdot 8 \cdot \overline{24} \cdot 5\}$.

Thus the evolution of the forms of the calcite can be explained by a decrease of the supersaturation in the mineral-forming solution with passing time. And because the light carbon isotope content changes in this process, the conclusion can be made that the isotopic composition of carbon in the solution is a function of solution supersaturation. And this, in turn, depended on the carbon dioxide content of the solution. In other words, calcite precipitation was determined by the ratio Ca^{2+} in the solution. Rhombohedral-prismatic calcite crystals settled down from the solution supersaturated with respect to carbon dioxide. As soon as the supersaturation dropped, the calcite habit gave way to a rhombohedral one and then to a scalenohedral. This appears to have taken place simultaneously with the solution becoming more alkaline. Thus if the dissolved carbon dioxide became less active (a decrease from 10^{-1} to 10^{-6}), the activity of calcium ions remaining the same (10^{-1}-10^{-6}), calcite synthesis occurred when the pH of the environment rose from 8.3 to 10.8.

Pure natural calcite occurs as colourless crystals. More frequently, however, calcite crystals contain impurities and are hence coloured variably. According to the mineralogist V. Sergeev, brown calcite is always related to relatively high concentrations of manganese and iron ions in it. Little manganese and iron is present in greenish-yellow calcites. Widespread yellow colouration is due to the CO_2^--groups located near manganese ions that have isomorphously substituted for calcium ions in the carbonate lattice.

Absolutely black calcites have been found, the causes of this colouration being diverse. Thus, the calcite from the western United States is black because of impurities of some metals, in particular zinc, lead and silver. The coarse-grained calcite was found to contain 43 g/t silver. The black calcite from the Kafanskii ore district, Armenia, was coloured by a mechanical impurity of psilomelane. Rather scarce are pink and purple calcites. The colouration of the former is due to a high manganese ion content and that of the latter, ferric iron in the structure of calcite.

The calcite crystals from sulphur deposits are colourless, water transparent, yellowish, light and dark brown, or black. The amount of manganese is nearly an order of magnitude higher in the light-yellow calcites from the Rozdol'skoe and other deposits than in colourless crystals. This suggests that the calcite is yellow owing to bivalent manganese, which compensates for a calcium oxide deficiency in the carbonate.

The brown and black colouration of a calcite is of a different origin. The point is that calcite is generated in a wide range of geochemical conditions and is one of the matrices on which organic molecules are transformed in nature.

Calcite crystals easily sorb organic molecules. In other words, calcite always contains organic matter caught by the crystal while growing. Thin sections of dark-brown crystals show that both outer and inner parts are coloured intensively. This allows one to disclose the zoned structure of calcite polyhedra and the features of their growth namely the origin and disappearance of faces, and their traces after their dissolution. Besides the zoned colouration, mottled and flowing colourations are observed.

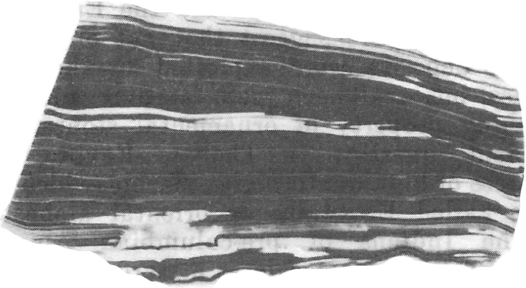
The greatest amount of organic matter was found in granular calcite aggregates from the sulphate and carbonate rocks of the Dnieper-Donets depression. The calcites range in colour from dark to absolutely black. The pigment is mainly restricted to the periphery of grains and slows down their growth along [0001].

Ornamental Calcite

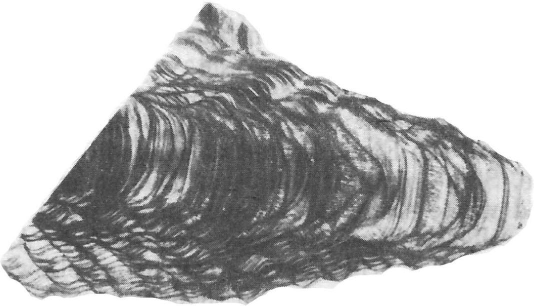
Ornamental calcite was noted in the Gaurdakskoe sulphur deposit and in the nearest regions. Especially interesting are onyx marble and the ornamental calcite proper.

Onyx marble. Wonderful objects made out of this stone have been widely used in designing the interior of temples and palaces, and in mosaics. The well-deserved good reputation of onyx marble was created by its banded or concentrically layered pattern, vitreous lustre, and soft, pleasant tinges of milk-white, amber-yellow and brown colours. Furthermore, the stone is attractively translucent to 3-4 cm inside and so has been used since long ago to make various objects but rarely to produce ornaments. Onyx stands for Greek nail because of its layered structure, radiance and soft colours. Commonly, however, onyx is taken to mean thin-banded agate with alternating white and dark layers.

Onyx marble was one of the stones beloved by some peoples. A legend says that Solomon's Temple in Jerusalem had no windows but remained light even when the doors were closed. This was because the walls of the temple were built of onyx marble translucent to sun light. In Ancient Egypt, onyx marble was used to make statues, sacrificial plates, sign posts, vessels for storage of aromatic oils and other stuffs, cups, lamps and other temple implements. Astonishingly fine is one of the lamps found in the Tutenkhamon tomb. Its arms are in the form of hieroglyphs meaning unity and eternity. When the lamp shines, images of



Alternation of white and black bands in onyx marble



Honey-yellow calcite jets in onyx marble

Pharaoh and his wife, flower garlands and other figures were seen on its walls. Another lamp was carved as lotus flowers on one stand. The Mesopotamians used onyx marble as early as the 5-4th millennium B.C. The findings of art of Ancient Egypt and the Euphrates-Tigris interfluve suggest that not only gemstone deposits were exploited in those old times, but craftsmen were familiar with the shaping property of ornamental stones. The ancient quarries in Thebes, Egypt, were sources of high-quality onyx marble, which was also called Egyptian, or oriental alabaster.

The Indians of pre-columbian America referred to onyx marble as a sacred stone and willingly carved cult objects out of it. This ornamental stone has long been loved and honoured in Mexico, ancient India, and the countries of the Near East and Middle Asia.

In putting into practice the idea of building architectural ensembles, Timour and Ulugbek used onyx marble to construct magnificent buildings we can see nowadays. Nice greenish onyx marble decorates the walls of the Timourides' Gur-Emir tomb in Samarkand. Many poets of the East referred to banded onyx marble. Some of them compared this smart black and white stone to the eyes of a gazelle or a sweetheart. Exceptionally beautiful is Algerian onyx marble having a gentle yellowish-green colour. It was used to decorate the balustrade of the main staircase in Grand Opera, Paris. The Kievskaya, Belorusskaya and Dynamo underground stations in Moscow are faced with onyx marble. At the Belorusskaya Radial underground station, onyx marble plates were used successfully to decorate the lamps.

Major onyx marble deposits are known in Algeria, Pakistan, Afghanistan, Mexico, USA, Italy and Argentina. In the USSR, much onyx marble has been discovered in the Lesser Caucasus Mountains and Soviet Central Asia. The Karlyukskii deposit is most famous among those in Soviet Central Asia. The Karlyukskii Caves of the Kugitangtau Range were noted even in the "Historical Library" of the ancient Greek scientist Duodorus, who lived in the first century B.C. The Gaurdakskoe onyx marble occurrence has recently been discovered. The Karlyukskii deposit embraces several caves, for instance the Khashm-Oyuk, Kap-Kotan and Festival'naya, confined to the Oxfordian limestone suites, the western side of the Kugitangtau Range.

As soon as geologists found onyx marble in one of the Karlyukskii caves, a legend about a rich hidden treasure came back to the old residents of the Karlyuk Village. Sleeping Dragon—a mythical creature endowed with a supernatural strength, and having a long scaled body, terrible claws and a fire-throwing head—was tireless in watching over a hidden treasure. Grey-bearded elders were told by their grandfathers that once upon a time the emir of Bukhara famous on the East and outside for his riches and exceptional cruelty wormed the secret of underground riches and felt like to take possession of them. But that's not how it turned out! The kind Owner of Mountains didn't want to give back gemstones to the greedy and treacherous emir. He brought down the vaults of underground storerooms, displaced and intermixed stones, hid treasures again and ordered Sleeping Dragon to better watch over them ... .

This is the legend that can be told you even now by the elders of the Karlyuk Village in the mountains if you go there to examine caves and see onyx marble in them. But each legend contains a grain of truth, and this was confirmed by stone lovers, speleologists and geologists who have recently discovered several onyx marble occurrences in the region, such as the Srednee, Esh-El, Bumak-Dara, Tash-Yurak and Promezhutok.

To see how the onyx marble occurs in the Khashm-Oyuk cave, you should descend into a karst cavity to a depth of about 100 m. While descending you should overcome a slope of approximately 20°, pass over loose deposits and a pile of huge stone blocks resembling ruins of an antique town. You can force yourself but with difficulty between these blocks. Throughout years of tireless work in the darkness of the interior as an architecture and builder, dissipating water has created a giant labyrinth more than 5 km long. By opening up its phantasy, the Nature has built up in the underground palace grottos resembling true halls with whimsical columns 20 m high, and decorated them with intricate cornices, openwork arches and balconies. The cave is dry inside. The underground kingdom of water and stone, wonderful stone falls of gypsum and onyx marble are like a fairy tale in which the Night reigns once and forever.

The visitor is tightly surrounded at once by wet darkness and winding labyrinths. The light of an electric torch scanning the sparkling surface of numerous faces of crystals on the walls distinguishes from the darkness stalactites and stalagmites, and stony blocks resembling animals. Look at the silhouette of a huge animal against the darkness: thick legs, a massive body, a trunk grown on to the cave floor, and a small tail. This stalactite group is called "Elephant". Then the light of the electric torch catches out a "Cross" from the darkness. And all these are made of white gypsum, as are the whole wood of stalactites—trees without boughs, hollow inside. The gypsum crystals growing on the cave walls resemble leaves, flowers and man-made lace patterns, as if a mysterious sculptor walked along the cave and disappeared in the eternity. If you go along a dark pass alone, the gloom is overcome only just in front of you and thickens at once behind of you. It seems to you, as if you carry the space open to sight with you. In making your way along a narrow pass, you feel mighty rhythms of stone masses, the stability and, at the same time, illusoriness of the cave, the beauty and harmony of the world not only on the surface but also in the interior of the Earth.

In the Karlyukskii caves, onyx marble makes up sinters (crusts), up to 1 m thick, on the walls of passages and the floor of caves. The crusts are hummocky, occasionally looking like giant paws, a stepped waterfall, a bunch of grapes and other whimsical figures. Typical onyx marble stalactites are scarce. Hanging from the ceiling are not only massive sinters in the form of drapery and fringed curtains as long as 4 m but also peculiar crystal intergrowths as giant chandeliers and trees with their crowns directed downwards. The cave floor is covered by stalagmites ranging in diameter from several centimetres to half a metre and up to 2 m high. The truly magic beauty of the Karlyukskii caves attracts speleologists and tourists.

The onyx marble from the Karlyukskii caves is calcitic. It can be regarded as typical of this ornamental stone. It is coloured white, yellow, cream, brown and honey yellow, and is patterned, transparent or semitransparent, which makes the layered pattern especially expressive. The onyx marble with translucent 1-mm thick brown and white bands is surprisingly beautiful. Attractive are samples with whimsical wavy and concentrically zoned bedding of white, light-brown and brown calcite, the layers ranging from tenths of a millimetre to 1 mm.

The onyx marble extracted from karst caves has until recently been treated in Dushanbe. Its blocks were raised from the caves, sawn into numerous plates and treated on a machine.

The result was a material with spectacular banded patterns of different colours, which was used to make boxes, desk sets, stands for desk lamps and souvenirs. Vases having a wavy pattern were cut out of large pieces. The stone was extracted uneconomically, however, and the Karlyukskii mining district was closed soon.

The Gaurdakskoe onyx marble occurrence is located in a karst cave at the sulphur deposit of the same name and in the fracture zone of the Gaurdakskoe uplift. The karst cave, which was exposed in a quarry in 1973, was formed in the upper part of bituminous limestones in the Kugitangskaya Formation (Oxfordian), and in limestone and gypsum-anhydrite in the Gaurdakskaya Formation (Kimmeridgian). No sinter crusts of onyx marble have been found on the walls and floor of the cave. It occurs in unattractive stalagmites that rise as various-size poles from the cave bottom. Its deposits are thinner than those of the Karlyukskii onyx. Especially many stalagmites have been found on the floor of an inclined pass called the Oniksovyi. The thickness of deposits of this ornamental stone depends directly on that of the enclosing limestone.

The onyx is of calcitic composition; it is coloured dark brown and light to dark honey yellow. White, yellow, golden-yellow, cream, pink and brown bands alternate with gradual transitions and produce, together with the fibrous calcite structure, a fine, graceful pattern. The stone is rather compact, and is easy to split and cut to form a mirror surface. It is translucent to some depth, resembling a miracle vessel filled with spring water.

As compared with the Karlyukskii onyx, the Gaurdakskii onyx is more silky and markedly darker. The onyx in pointed stalactites has an especially pleasant silky lustre. Polished specimens show a fantastic interweave of extremely fine streaks of all brown tinges. The onyx marble from stalagmites capped by gypsum crystals is less patterned. Pendants with a graceful, never repeated pattern are especially beautiful from this translucent onyx. Mysterious light carried, so to say, from deep in the Earth is seen in them.

Within the Gaurdakskoe uplift, deposits of onyx marble are restricted to fissures, as wide as 15 cm, cutting the Upper Jurassic limestone. Its structure here resembles a fossil tree: white, discontinuous, thin layers of parallel-fibrous calcite are against a dark background of dense fine-grained calcite. The polished sample is coloured deep brown; only thin plates are translucent. As compared with the onyx from the caves, that from fissures is better from a commercial point of view; it is harder and more viscous and looks lovely after polishing. It is cut to produce boxes.

The onyx marbles from the caves studied contain approximately the same amount of chemical elements. These in the Gaurdakskii onyx are zinc, chromium, copper, barium, strontium, lanthanum, zirconium, titanium, aluminium, silicon, magnesium, calcium, sodium, iron and manganese, and in the Karlyukskii onyx, also nickel and molybdenum. The contents of titanium, aluminium, silicon, manganese and organic matter, responsible for the brown colouration of the samples, are higher in the Gaurdakskii onyx, whereas those of zinc, chromium, barium, zirconium, magnesium and iron are higher in the Karlyukskii onyx. The better coloured, dark-brown onyx from Karlyuk is rich in sodium and iron, and the white onyx, in zinc.

The beauty of onyx marble depends not only on its colour and patterns but also on the degree of its being translucent. It is the higher, the deeper lies the onyx. Light iridescence makes onyx and objects made out of it especially attractive.

Onyx studies under the microscope have made it possible to disclose the nature of its translucency. This valuable property is due to the internal structure of the aggregate, above all to similar in size and shape fibrous calcite crystals whose optical orientation is approximately one and the same. The thin fibers of calcite and their aggregates thousandths to hundredths of a millimetre across are elongated in the direction of their growth towards drops of carbonate solution falling from the ceiling. Besides the fibrous calcite, transparent crystalline calcite also precipitates from solution. It binds the fibrous aggregates into a single whole. A rapid alternation of variously coloured, translucent bands of fibrous calcite has an effect of silky play in the specimen. Moreover, when passing through the stone, light is reflected from the minute faces of calcite crystals and hence becomes enriched in new colours.

With the increasing size of calcite fibers, the quality of onyx marble decreases perceptibly. The stone becomes dim, being translucent only in thin sections, and lacking its inherent pattern. In pores, little fibrous calcite crystals grow under favourable conditions, reaching 1 mm in cross-section. Their crystallization is not accompanied by transparent calcite deposition. These segments have no ornamental properties at all and are hence rejected.

Onyx marble is derived from precipitation of calcium carbonate (calcite) from waters circulating in limestones. Carbon dioxide plays a decisive role in this process. Carbon dioxide-bearing water can dissolve limestone (calcite solubility in pure water is 13 mg/l at atmospheric pressure and 16 °C). Calcium carbonate is then converted to hydrocarbonate by the reaction

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$$

The solution is stable only if it contains an excessive amount of the dissolved carbon dioxide. The greater the excess, the more lime is dissolved in the water. When the carbon dioxide escapes from water, Ca^{2+} and HCO_3^- are combined into insoluble calcium carbonate. A similar process takes place when hard water is boiled in a kettle. Excessive carbon dioxide is removed from the boiling water together with steam, while lime is laid down as a scale on the bottom and walls of the kettle. A chemical reaction opposite to that leading to calcite dissolution occurs in both cases.

The bulk of calcite settles down under a thin film of water that streams over the ceiling, walls and floor of the cave. The shape of a newly formed carbonate material depends on the way of streaming of the calcium bicarbonate-saturated water. If the water seeps through a crack in limestone and runs down the wall, a sinter appears on it. This is the way in which onyx marble originates in the caves of the Karlyukskoe deposit. If the drops fall from the ceiling, a stalactite will grow here in due time. If the drops are not kept on the ceiling but at once fall vertically on the floor, the patch on the floor will grow into a broad sinter, stalagmite. The highest carbonate stalagmite, 29 m high, was found in the L'Avene Cave, France. The longest stalactite (59 m) is supported by the wall of the De Naria Cave near Malaga, Spain; it has grown down to the floor.

Ornamental calcite. In examining the Gaurdakskoe sulphur deposit, we paid attention to the fact that sintering calcite aggregates are widespread in the vicinity of Gaurdak, these having a banded or concentrically bedded pattern in which light calcite bands alternate with dark and grey ones.

The outer appearance of calcite sinters is unattractive: they are grey, earthy grey and dark coloured. The surface is hummocky, covered with dust and hence looking very much like common limestone. The stone is easy to cut, grind and polish with the formation of a mirror-like surface that may survive for decades. And each sinter exposes its own, unique combination of grey, cream, medium-dark and reddish brown colours. If a plate of sintering calcite is cut not parallel to bedding but somewhat obliquely, the layers will appear as rings, complex loops and intricate figures. Quite beautiful are polished plates with numerous concentric rings. These rings are spherical segregations that have either a regular or a distorted shape of a ball and a concentrically zoned texture resembling that of agate. The light-coloured thin bands of concentric rings are mostly fine-grained calcite, while the dark ones, parallel-columnar, that is closely intergrown, thin (up to 1 mm) calcite crystals bounded on their sides by uneven planes. As compared with the earlier-described onyx marble aggregates, which have a lovely amber-yellow colour and are translucent, the calcite under study is darker. It contains 0.5% Fe + Mn + Ni, and also organic matter.

Sintering calcite precipitates from cold water, particularly from calcium bicarbonate-saturated, finely dispersed solutions flowing slowly over the uneven surface of limestone. Calcium bicarbonate is unstable under common conditions: when the internal pressure drops, it decomposes easily with a carbon dioxide evolution and calcite precipitation. Each calcite layer is deposited from a separate solution batch. Impurities in the solution are responsible for a thin banding of the calcite laid down and for its varied colouration. Thus, ferric iron imparts a greyish brown-yellow colour to crystallizing calcite, while organic matter makes it dark coloured. The calcite is also affected by small amounts of manganese and nickel, which colour it cream and light grey, respectively.

The fine-dispersed material of sinters also contains clay. When sinters are formed, the clay minerals in them undergo certain alteration, but no one still knows what it is in particular. The transformation of clay minerals along with the recrystallization of finely dispersed carbonate material may change the initial configuration of sinters.

The ornamental merits and easy treatment of calcite allow its use in stone cutting.

A Mineral of Vital Importance

Rock salt has been an integral part of man's everyday life since times immemorial. It is called simply salt in domestic life, sodium chloride in chemistry, cooking salt in engineering and halite in mineralogy.

The notion of the mineral halite is complicated. It depicts natural sodium chloride crystal that occur almost invariably as cubes, though its symmetry class allow some other forms to occur. Halite crystals can be as large as 10 cm along the edge of the cube; they were found in both old and modern sediments, separately or together with other minerals.

Rock salt was essential not only in the economic but also in political life of peoples; it was the object of exchange and trade, and a good source for replenishment of state treasury. Salt was a cause of bloody wars and people's uprises and riots. The Roman historian Tacitus (ca. 58-117) describes a murderous battle between hettas and germandures for salt possession. The salt mines in the mouth of the Tiber River were the objects of continual wars between the Romans and the neighbouring tribes.

Duties and taxes were first imposed on salt in China, Japan and India several thousand years ago. Salt taxes were later enacted nearly in all countries of Western Europe and in Old Russia. Instead of small duties, the tsar government imposed a single tax—two grivnas a pud (16 kg)—on salt. Then the salt, which was dear all the same, became twice dearer, and this caused people's discontent. A three-day salt riot broke out in Moscow in 1648. It triggered unrest in Sol'vychegodsk, Ustyug Veliki and Solikamsk. Concerned with the riots, the government had to abrogate this too high salt tax. Similar riots also occurred in other countries. In the 16th century, a true armed uprising flared up in the French port La Rochelle, through which salt trade was conducted with many oversea countries. Two days of battles in the streets ended with a defeat of the insurgents. An uprise of China peasants arrogant with salt taxes lasted nine years in the Middle Ages. Its interesting description can be found in B.Ya. Rozen's "Salt crystals".

Salt has long served as the main unit of exchange in Central Africa, some regions of the Sahara Desert, on New Guinea and in several other places. It was used to pay for trade duties in some European countries in the Middle Ages. The crusaders were sometimes payed by salt. The Roman legioners received salt for their service even earlier. It is suggested that the word soldier is related to salt, it is a derivation from the Latin "solidus", a coin. Possibly, the English "salary" and Italian "soldi"—small coin—are of the same origin. Salt was once dearer than iron and silver, as dear as gold. Even Cassiodorus (the first half of the 6th century), the secretary of the king of Ostrogoths, said not without reason, "Salt is necessary for everybody, though many can do without gold."

The uncomparable taste of salt has been known for a long time. Salt is a component of all dishes, even of sweet cakes! But salt is not only the crucial food stuff; perfect metabolism, normal life activity of man and animals are impossible without it. Salt regulates the work of heart and muscles, is present in gastric juice and bile, and is a constituent of blood, That's why African hunters and residents of Arctic coasts drink the blood of the animals they just killed. The blood plasma contains the greatest amount of salt. So the small white crystals we see every day and put into food can be called a mineral of life. We intake 20-25 g of salt a day, and but 200 g of this stuff is in our organism.

Rock salt has numerous applications. Its main consumer is chemical industry, which uses not only the salt itself but also sodium and chlorine, its constituent elements. Salt participates in a great many reactions to produce various compounds.

Rock salt is often used as a medicine. Pliny the Elder wrote that salt relieves and cures nervous sufferings, the pain in shoulders and loins, a stitch in one's side and colic in the stomach. Today's opinion on the miraculous properties of this mineral is less optimistic, but medical men know that salt miners never suffer from bronchial asthma and are rarely ill with flu, or catch cold. That's why underground clinics and sanatoria are created in the openings of salt mines. Temperature, humidity and pressure are constant in them years around, but the main thing is that no microorganisms causing allergic diseases, including asthma, are present there. The air contains much rock salt vapour; patients take no medicines, all procedures are at a minimum. When you are in sterile, bactericidal air, your body becomes stronger, more resistant to sickness. Those who suffer from bronchial asthma are cured of hoarse coughing and suffocation paroxisms. And it is all thanks to the curative air of salt mines. An underground sanatorium was founded in the salt mines at Wieliczka, Poland. In the USSR, underground hospitals function in Solotvino, Transcarpathians; in the Kirgiz Soviet Socialist Republic and in the Nakhichevan Autonomous Soviet Socialist Republic.

The underground space left behind after rock salt mining is also valuable in another respect. It serves for storage of gas and petroleum products.

Rock salt is easy to treat. Thus an underground cathedral sawn out of salt is known in the vicinity of Bogotá, capital of Columbia. It occupies nearly the same area as Notre Dame de Paris. This cathedral is acoustically perfect, hence, musical concerts often take place there.

A valuable remedy is bishofite, hydrous magnesium chloride, a bitter "relative" of rock salt, which is the end-product of brine drying. Small colourless bishofite crystals are very easy to dissolve; they take moisture even from the air. The geologist E. Novikov says that concentrations of this mineral were discovered near Volgograd several years ago. Greyish sand was lifted to the surface from a depth of about 1 800 m, and a wet spot was the only stuff left behind in some time. It has been found that a 70-m bishofite unit lies among compact, air- and water-tight rocks. This sensitive mineral cannot be mined;

it is extracted by the method of underground leaching. Each cubic metre of bishofite brine transports to the surface 450 kg of magnesium chloride. The brine is used to obtain not only magnesium but also bromium, boron and other valuable components.

Extremely vast basins of salt deposition occupied in the past large expanses of Europe, Asia, America, and continental shelves next to the Atlantic and Indian oceans. These seas disappeared long ago; instead, we can see now thick beds of rock salt.

Much salt is dissolved in the World Ocean. Specialists have calculated that if all of a sudden the water of all seas and oceans evaporated, the salt deposited would be enough to build a wall, 1 m thick and 280 m high, that would encircle our planet along its equator.

The salt content of sea water is, on average, 3.5% (it varies from ocean to ocean but is rather persistent within a large basin). The salinity is always higher in open sea than near sea shores.

The European salt deposits were generated more than 200 m.y. ago. Ocean water invaded there from the northwest at that time and flooded rather vast territories of Middle and Northern Europe to form a shallow, so-called Zechstein sea. This sea included the basins where salts were deposited. The climate in Europe was hot and dry, so the Zechstein sea evaporated rapidly, and the components dissolved in it precipitated in the order of their solubilities (limestone, anhydrite, rock salt).

Readily soluble potassium salts were laid down on the rock salt at the time of prolonged interruptions and introduction of new sea-water batches. This was the way of gradual formation of salt masses, which were later overlain by younger sediments.

The World Ocean has a constant salt composition: 99.9% of total salts in the ocean are made up of only eight components (in %): 55.04 chlorine, 30.61 sodium, 7.68 sulphate, 3.69 magnesium, 1.16 calcium, 1.1 potassium, 0.41 hydrocarbonate and 0.19 bromium. But did it always remain the same? Academician A. Yanshin believes that the total salinity and dissolved-salt composition of the World Ocean has been undergoing substantial changes for the past 570 m.y. If so, the data on salt precipitation from modern sea water are hardly to be extrapolated back to the far geological past of our planet. In A.L. Yanshin's opinion, minerals or their combinations in the evaporites can be quite helpful in reconstructing the geological history of the Earth.

Salt Domes

Not all huge rock salt masses occur as approximately flat-lying beds of varied thicknesses. Some salt deposits are dome-like; their base lies at 5 to 8 km of depth while their apices rise to the surface, sometimes even above it. The domes originate in the following ways. Salt becomes plastic at high temperatures and pressures in the Earth's interior. But because the heat expansion coefficient of salt is higher than that of other rocks, it expands greater and is ultimately squeezed upwards. The salt "flows" in the direction of the least resistance, intruding the overlying rocks. The case for the above said is, for instance, the salt-bearing units in the Dnieper-Donets depression are heated that to 100-175 °C. It is suggested that the mother salt bed on the Gulf Coast occurs within the 200 °C zone.

Salt domes originate in weakened crustal segments, particularly at fault intersections. A dome consists of a salt mass (plug) and an overlying structure of turned up strata. Major salt domes are known in many regions of the world. In our country, there are many salt domes within the Near-Caspian depression and Dnieper-Donets depression. They were also found in the FRG and USA. On the Gulf Coast, USA, the salt domes range in area from 1 to 500 km^2, extending to a depth of 11 km or more (the roots of some plugs have not been tapped).

The highest, that is exposed salt domes in the USSR occur in Tadzhikistan. One of them, the Khodzha-Mumyn (Salt Mount), is near the town of Kulyaba. The dome overlooks the surroundings by almost 900 m, resembling in appearance a giant white helmet with a bump. More common are low domes or even those concealed by soil. Lakes are located on some of their flat summits covered with clayey deposits. The widely known Lake Baskunchak, more than 100 km^2 in area, is precisely of this origin. The lake is no more than half a metre deep. Water evaporates in summer and autumn, leaving dazzling white salt on the bottom.

Really sensational were findings of salt domes in the abyssal basin next to the continental slope of Western Africa. The salt-bearing materials pierce through the sediment and approach the Atlantic floor extremely closely; some of them even make up mounds on the floor as high as 225 m. These structures are similar to the salt domes beneath deep waters of the Gulf Coast. The salt is late Triassic to early Jurassic in age (about 150 m.y. old). It appears to have been accumulated in a narrow crevice, as in the modern graben of the Dead Sea. Since the area of distribution of salt domes is rather extensive, the respective depression could have been very large. A perplexing problem that should be solved by scientists is the mode of origin of salt domes beneath the Atlantic floor. Its solution would be of great practical importance, because rich oil and gas deposits are confined to salt domes on the land and continental shelf.

Salt domes are interesting not only because of their structure but also for their economic value. The sulphur production in the capitalist world comes mainly from the salt domes in the USA and Mexico. In the United States, the region of salt domes extends along the

Gulf Coast from the Rio Grande River eastwards through Texas, Louisiana and Mississippi to Alabama. The main sulphur belt intersects eastern Texas and western Louisiana. The productive beds lie in the depth range from 400 to 800 m. The sulphur-bearing bed is, on average, 30-40 m thick, at places much thicker. The rocks contain 10 to 70% S. In Mexico, the native sulphur production is restricted to the Tehuantepec Isthmus. The sulphur content of rock is there as high as 33%. Commercial sulphur bodies occur in the caprock of salt domes. A caprock is taken to mean a complex carbonate-sulphate geological body left behind after the salt plug was gradually dissolved. It is as a puzzling rock as a salt plug.

Not all understand why curved crystals and drop-like segregations of sulphur occur in small cavities in salt. Here, the space free of sulphur is filled with a brine containing a perceptible amount of hydrogen sulphide. If you break up or split up a lump of sulphurated salt, this gas will escape into the air, and its containing liquid evaporate rapidly. Judging from a strong hydrogen sulphide odour, the concentration of this gas in the salt is rather high.

The curved sulphur crystals are similar to the polyhedra described in the salt, but their edges are rounded and faces are convex. The rounded forms resemble drops of first molten and then solidified sulphur. Most of them, however, retain relics of natural faces. The surface of rounded crystals is bright and glossy; they are coloured pale yellow to dim white. It is quite possible that these were formed from well-developed sulphur crystals at a high temperature. The partial melting of sulphur crystals depends on the temperature to which the salt was heated. The temperature rise in the salt unit could have been the result of basalt magma intrusion into the salt domes of the Dnieper-Donets depression.

The term caprock has been used in the literature since 1901, after a sensational oil discovery in the Spindletop salt dome, Texas, and the extraction of native sulphur at the Sulphur dome, Louisiana.

It was first thought that caprock had formed at the expense of limestone and anhydrite that overlie the salt unit. This suggestion was rejected, however, because no bedding had been found in the caprock. In the first decade of the 19th century, German scientists tried to account an anhydrite cap present on some salt domes on the North German basin for the residual material of the salt unit itself. But this point of view was accepted only in the 1930's. Arguing against this mode of caprock origin, many scientists referred to the small amounts of residual material in rock salt and to the unfavourable conditions of circulation of salt-dissolving water. And only detailed studies of the American petrographer D. Brown did confirm the residual nature of caprock's anhydrite.

The domes of salt plugs occur at different depths. Some break through the overlying sediment, and the rock salt crops out; others are buried at great depths. The salt plugs are divided into shallow (up to 900 m from surface to dome) and deep (more than 3 km).

Considerable salt masses are moving even now. They are marked at the surface by topographic highs and lows, springs of acid or hydrogen sulphide water, gas and oil show, and enhanced salt contents of reservoir waters.

The internal structure of salt domes has been dealt with in a number of publications. The Palangana dome is a characteristic example. It is slightly oval in shape, its size being 2.4 × 3.2 km. The strata dip at about 70° and strike chiefly northwest—southeast. They consist of four lithified formations, the San Diego, Palangana, Benavides and Anhydrite. The first two are halite in composition. In addition, the San Diego contains sand interbeds and the Palangana, grey and pink sylvite beds. Appreciable anhydrite is present in the Benavides halite. The anhydrite is named after the respective mineral much of which is disseminated in the halite. The interbeds, composed of anhydrite streaks, scales and fragments as large as 5 cm or more across are up to 1 m thick. Owing to local dislocation, the anhydrite beds are crushed and separated into blocks. This description suggests the vertical zoning of the salt domes.

In contrast, caprocks show three flat-lying zones, the anhydrite, the transition and the calcite (limestone); these are present invariably, with some exceptions, where the caprock is sufficiently thick whatever the presence of sulphur in it.

The anhydrite zone directly overlies the salt, which is either porous, cavernous or massive, granular; it covers the whole salt bed. This zone is due to a residual accumulation of water-insoluble minerals. The lower part of the zone is made up, at the direct contact with the salt, of loose anhydrite grains and other minerals of the insoluble residuum associated with the relics of salt grains. The cavities in the salt are filled with salt solution and loose accumulations of anhydrite grains. On anhydrite dissolution, the insoluble residuum becomes more and more compact.

The anhydrite in the lower part of caprock is rather massive; it consists of strongly cemented grains of this mineral producing a "brick pile" structure. Upwards from the contact with the salt, the anhydrite rock grades into a typical massive saccharoidal anhydrite. The degree of disturbance of the anhydrite rock increases in the same direction.

The anhydrite grains in the zone are akin to those in the salt and differ drastically from those in the primary sedimentary anhydrite beds. A characteristic feature of the anhydrite rock is that it is very coarse-grained and contains chaotically arranged dolomite rhombohedra, and quartz crystals and rosettes. The primary anhydrite is usually very fine-grained, with veinlets and interbeds of calcareous and clayey materials and with some calcite and dolomite grains less than 0.01 mm in size. The anhydrite rock of caprocks also contains quartz sand lenses and sandstone fragments similar to those in the anhydrite beds.

The accumulation of the anhydrite unit against the background of rise of the salt and caving of the caprock under formation favours not only deposition of anhydrite but also its deformation and brecciation, particularly noticeable in the upper part of the zone. Here, immediately under the transition zone, the anhydrite is often fibrous and thin-bedded. It frequently shows traces of brecciation and flow. The brecciated anhydrite is composed of variously coloured anhydrite fragments. Deformed are also many dolomite and quartz crystals. The compaction and deformation of the anhydrite rock are accompanied by another process—recrystallization of anhydrite during which its large grains grow at the expense of small ones. Parallel to this, the mineral gets rid of impurities.

It should be borne in mind in studying anhydrite residuum accumulation that the solubility of anhydrite rises, though insignificantly, with an increase in the common salt content of the solution. Hence it should be accepted that some anhydrite has been at least locally dissolved. As should be expected, this process was most intense in thick caprocks, where the salt dissolved rapidly, whereas the concentration of anhydrite was insignificant.

The transition and calcite zones were derived from anhydrite alteration. The appearance of the transition zone coincided with entering of liquid hydrocarbons into anhydrite and with the resulting sulphur formation. This zone results from accumulation of much anhydrite. It grows downwards from the caprock top and is irregular in shape—somewhat thicker at the sides of the caprock than at its centre. Besides the anhydrite zone proper, isolated blocks of anhydrite have been noted inside the calcite zone (Big Hill, Jefferson Island, Lake Washington and other domes).

The transition zone contains newly formed minerals. The principal minerals of the zone are gypsum, calcite and sulphur. Abundant water circulating in the caprock favours anhydrite transition into gypsum. Fine anhydrite grains converted to gypsum intergrow into large irregular aggregates with an identical optical orientation of their constituent grains. When gypsification preceded the transformation of anhydrite into sulphur and calcite, the sulphur-calcite aggregate grew further after gypsum. Secondary gypsum (after anhydrite) is found at depth; it is common in disturbed rocks or nearby, and has been found close to the surface (Winfield dome) and at a depth of 610 m (Garden Island dome). But more often than not, the secondary gypsum is generated below 300 m of depth.

Gypsum and anhydrite replacement by

sulphur and calcite has been noted throughout the transition zone except the blocks of compact, undisturbed anhydrite lying just above the salt.

The newly formed calcite occurs as small scalenohedra, and sulphur, as small grains. Both form a sulphur-calcite aggregate that retains minute details of the mineral under replacement (orientation of cleavage joints, structure of the surface and so on). And if the anhydrite have earlier been hydrated into gypsum, sulphur and calcite that replaced it preserve all details of the mother sulphate. That the anhydrite is more frequently transformed into gypsum than into calcite and sulphur is due to its having more cleavage planes than gypsum and hence being easier for solutions to penetrate. Close relationships between sulphur and calcite suggest their simultaneous formation after anhydrite. Disseminated sulphur predominates in orebodies. Calcite and sometimes sulphur replace dolomite, barite and celestine crystals, which were added to the transition zone and subtracted from the salt unit.

The calcite zone overlies the transition zone and extends to a depth of several hundred metres. Besides the calcite, the rocks contain gypsum and sulphur, as well as relict grains and isolated blocks of anhydrite. There occur very fine- and very coarse-grained calcites. The former is a replacement of dolomite, barite, celestite and other minerals of the anhydrite zone, except quartz and pyrite. Thin calcite and also sulphur were simultaneously derived from anhydrite replacement. The calcite contains inclusions of black carbonaceous matter, and white and cream clay; it is at places penetrated with oil. The very coarse-grained calcite was found in veins cutting through the whole caprock.

If the sulphur is rather widespread in the transition zone, it is also enriched in the calcite zone, especially in its lowermost mass. Its upper most mass is porous and cavernous, unproductive. Little sulphur present here appears to have been replaced by other minerals, basically pyrite. Calcite, sulphur, pyrite and other sulphides, barite and celestite veins have been noted lower in the section. The calcite zone is at places severely brecciated. Redistribution of carbonate material, with its subsequent cementation with secondary calcite, is observable in the disturbed areas.

Deviations are seen from the described caprock zoning, owing to a complete or partial missing of zones. The calcite (limestone) zone occasionally lies directly on the anhydrite or is included in the anhydrite zone as various-size blocks. Domes with a thick caprock consisting predominantly of pure limestone occur both in Louisiana and Texas. Thus the caprock of the Humble dome (Texas), which covers the horizontal surface of salt and extends to depths ranging from 330 to 360 m, is exclusively composed of limestone. In contrast, no limestone zone is present in the caprock of the Stratton Ridge dome. At the same time, the caprocks contain appreciable quantities of deposits having nothing to do with the sulphate-carbonate rocks; also, sand and clay interbeds have been found in several caprocks. Finally, the anhydrite bed in the caprock of the Stratton Ridge dome is intercalated with sand and limestone.

In addition to its zoned structure, the caprock displays different types of secondary stratification. Salt plugs are chiefly bedded vertically, which, as some think, is due to an upward salt flow. This is proved by the elongate shape of halite crystals in the salt mass, and by other evidence. It would seem that the strata orientation should remain approximately the same in the caprocks. But the different-composition salt beds are here flat lying. This stratification can be observed in very coarse-grained anhydrite, in which it is due to rhythms in the precipitation of anhydrite grains from the salt. The bedding is intermittent both vertically and horizontally. Thin, indistinct, flat-lying, very fine-grained anhydrite beds, as thick as 1 cm, generally alternate with thicker beds of common, very coarse-grained anhydrite. This stratification is produced by dissolution of salt and subsequent compaction of the anhydrite grains released from it. Much is still unclear in the origin of this stratification, which is confined to the contact with the salt.

The second stratification type is observed in compact fine-grained anhydrite; it consists in an alteration of thin (about 1 mm) horizontal layers of dark-coloured, fine-grained anhydrite and thicker layers of light anhydrite. A close examination of this stratification has shown that it is observed in the primary (sedimentary) anhydrite that has been carried upwards by the salt.

An alternation of anhydrite breccia with white very fine-grained anhydrite can be mentioned among other bedding types. The caprock looks bedded because the sulphur and calcite veins lie horizontally.

In getting insight into the mode of caprock origin, of importance is the knowledge of water circulation in the sediments surrounding salt domes. The regions of salt domes are under hydrogeologically specific conditions. Salt dissolves in natural groundwater that is not saturated with sodium chloride. The waters flowing downwards and upwards first of all affect the top of the salt column (here the salt dissolves most rapidly) and then its sides. In this process, the peaked top of the salt plug is truncated, isoclinal folds lose their arches, and their surface then looks as that of a salt plug. The folds that were not dissolved by water are buried inside the caprock. The water that flows up the slope of the salt column dissolves salt not so rapidly; hence the caprock is quite thin at the sides of the dome.

The depths at which groundwater circulates rather actively while the residuum after salt dissolution is not removed from the top of the salt stock are most favourable for a thick caprock to accumulate. If the dome is where water circulates slowly, the respective caprock is thin or absent. The same is true if the water affected the salt during a short period of time, as in the Avery Island, New Iberia and Jefferson Island domes. The conditions favourable for the formation of thick caprocks were created at domes occurring relatively near the surface, where the groundwater circulation was sufficient for salt to dissolve rapidly.

The caprocks range in thickness from first few metres to 300 m or more, depending on the amount of salt dissolved, the overall content of the residuum and its mode of deposition. The absence of caprock on a shallow-depth salt dome is not due to a lack of residual material but because conditions are unfavourable for its build-up. Possible causes of thin caprock are cessation of salt plug growth or appearance of a layer screening the plug from circulating water. Finally, an intense rise of the salt stock may be responsible for caprock erosion, as at the Winfield dome; fragmentation, as at the White Castle dome; or separation, in its lower part, into bands, as at the Jefferson Island dome.

The caprock thickness varies because parts of the caprock may have been brought to erosion along faults. Caprocks are especially severely deformed and mixed up on small salt domes.

American specialists also describe so-called false caprocks. These are taken to mean a zone of cemented together sediments that are adjacent to a caprock, directly overlie it, or rest just on the salt body. A false caprock separates the caprock proper from the surrounding sediments. These are cemented with calcite, occasionally pyrite. Many calcite-rich zones extend from the caprock into the adjacent sediments. In Taylor's opinion, these are calcitized as a result of mixing of the salt plug-derived sea water with groundwater. After a false caprock has been formed, gypsum precipitates from the circulating solutions. Unlike common caprock, the false caprock contains fossil faunas, and a residuum produced by salt dissolution accumulates beneath it.

Let us compare the caprocks in the Dnieper-Donets depression with those on the Gulf Coast. We begin with discussing their profound differences. Clay minerals are substantial in the Dnieper-Donets caprocks. Furthermore, they contain fragments, among them blocks, or volcanic rocks, principally diabases. No rocks of this type have been described in the Gulf Coast caprocks. Another feature is that the Dnieper-Donets salt plugs are much more contaminated than the Gulf Coast ones.

The two regions, however, have some features in common. In both regions, the caprocks tend to consist of a lower, sulphate, and an upper, carbonate, zone. Unlike the Gulf Coast region, however, these zones are not very distinct in the Dnieper-Donets depression; they are somewhat blurred by a contaminating terrigenous-clayey material. Here also, the trend of relationships between the caprock and the salt plug is the same as at the Gulf Coast domes.

If we disregard the clay component, the caprocks whose chemogenic portion is exclusively sulphates, as at the Parafievskii and Logovikovskii domes, can be identified in both regions. The carbonates are subordinate in the caprocks of the Raspashnovskii and Dmitrievskii domes. In many caprocks, the chemogenic portion consists solely of carbonates. Even in the caprocks containing up to 80 % clay, the fragments of chemogenic rocks are distributed so that sulphate fragments predominate in the lower part and carbonate, in the upper part.

To summarize, the Gulf Coast caprocks are similar to the Dnieper-Donets ones. Sulphate rocks mostly occur in the lower caprock, and carbonate rocks, in the upper caprock. The amount of carbonates in caprocks markedly exceeds that in the salt. Both regions deviate from this trend. The mineral assemblages in the salt body and caprocks can sufficiently well be correlated between both regions. All caprocks are relatively rich in pyrite and contain dolomite; native sulphur tends to concentrate in the sulphate-carbonate rocks.

We have mentioned earlier that the commercial sulphur in the caprocks of American domes is restricted to the transition zone. Examples are the Sulphur and Big Hill domes. The sulphur-bearing bed is covered by a thin porous limestone bed. An anhydrite bed lies below it. No sharp contact is present between the beds. This occurrence of the sulphur-bearing bed was taken to develop a metasomatism hypothesis, whose main points were formulated by the American scientist Goldman. On the basis of relationships between the sulphates and carbonates, he concludes that the secondary processes here in action were due to intense anhydrite calcitization.

But this hypothesis is far from explaining the diversity of sulphur occurrences in the American domes. Thus, the sulphur in the caprock of the Bryan Heights is confined to gypsum which, according to the metasomatic point of view, must have been consumed for its formation. The caprock-overlying limestone contains no sulphur. Similarly lying is the sulphur body in the Damon Mound dome. The caprock contains as much as 50% sulphur, which is concentrated in gypsum-anhydrite. In the Palangana dome, the sulphuration has embraced the calcite zone of the caprock, but little sulphur has been found in clay and shale. It is interesting that uranium ores are localized in the sandstone of the Goliath Formation 30 m above the caprock.

A comparison of the minerals of the salt residuum with the accessory minerals of the caprock provides additional information about their origin. Taylor describes anhydrite (99% of salt residuum), dolomite, calcite, magnesite, ankerite, pyrite, marcasite, quartz, celestite, barite, borates (danburite, hilgardite, boracite), hematite, hauerite, kaolinite and quartz in the residuum of salts. Unlike the insoluble residuum, carbonates (calcite, dolomite, aragonite) are most common in caprocks. Pyrite is noted rather frequently; sphalerite and galena, more seldom; celestite, fluorite, quartz, barite and hauerite, even more seldom. As seen from the description, the carbonates prevail over sulphates in the caprock but do not in the plug; and here also new sulphide assemblage appears.

As mentioned above, the mineral assemblage that forms the salt plug and caprock has striking similarities in the domes of the Gulf Coast and Dnieper-Donets depression. The caprocks of both regions contain lead and zinc sulphides and fluorite, which are absent from the salt plugs. The presence of pyrite and dolomite is a characteristic feature of all caprocks. In all of them, sulphur tends to occur in the sulphate-carbonate complex.

It follows then that the caprocks developed identically in both regions, and hence the sulphur bodies in these caprocks are of the same origin. Most of the American authors relate the sulphur origin to sulphate reduction by organic matter. Under the action of hydrocarbons, the caprock sulphate is reduced to hydrogen sulphide, which is oxidized to sulphur immediately laid down here with calcite. As sulphur accumulates, the carbonate component of the caprock builds up as compared with that of the salt plug. All sulphur deposits occur where oil deposits or oil and gas shows are located. This suggests a genetic relationship between sulphur and oil.

As has been mentioned earlier, however, not all of the sulphur concentrations within the Gulf Coast and Dnieper-Donets depression are confined to the calcite zone of the caprock. This indicates that the hypothesis of metasomatism is not the only one that can explain the origin of sulphur and other minerals in salt dome caprocks.

Investigations show that the sulphur, pyrite, sulphate and carbonate of some caprocks were deposited by mineralizers rising from the roots of salt plugs. An example is afforded by the Adamovskii dome, which was examined by the geologist M.F. Stashchuk. According to him, the caprock limestones are not residual fragments but persistent interbeds forming a string of flat-lying, oblate bodies in the caprock. Such carbonate occurrence cannot solely be related to the generation of carbonate bodies in the already formed caprock, by mineralizers coming there from time to time.

That the carbonates and sulphates are added to the caprock is seen in the Lagovikovskii dome. The lithologist V.M. Stroev has found steeply dipping pyrite-calcite veinlets in the caprock, their thicknesses ranging from several centimetres to 3.5 m. Besides pyrite, the veinlets also contain chalcopyrite and specular iron. Together with pyrite, they constitute 35% of the veinlet.

The shape of pyrite crystals in the 357-604-m depth interval at the Adamovskii dome can serve as a mineralogical proof of the introduction of mineralizers in caprocks. In particular, the pyrite in the lowermost and uppermost parts of the section crystallized at a temperature somewhat higher than in the middle.

Finally, the rise of mineralizers from depths stems from the isotopic composition of native sulphur in caprocks. Thus, the $\delta^{13}S$ of fine-grained and coarsely crystalline sulphur varies in a narrow range at the Efremovskii dome, being equal, respectively, to $+17.5$ — 17.8 and $+17.1$ — $18.2^0/_{00}$. The averages of $\delta^{34}S$ for both varieties are equal to $+17.6^0/_{00}$. Another proof of sulphur input is its uniform isotopic composition throughout the caprock. This points to a single hydrogen sulphide source, while the composition would vary widely if the sulphur were derived from microbiological fractionation. The sulphur homogenization is a natural result of hydrogen sulphide coming from a single source.

This agrees with the sulphur occurrence not only in the calcite zone of the caprock but also in its other rocks that had had cavities by the time of input of mineralizers. Without mineralizing solutions, no sulphur originated even in those domes where the caprocks are made up exclusively of gypsum.

Searching for sulphur is now under way in that area of the Near-Caspian depression in which salt domes are located. Sulphur occurrences have been discovered in three domes in the western and central parts of the depression. The lack of information about the distribution of sulphate-carbonate caprocks, to which commercial sulphur deposits are generally confined, hampers finding sulphur-promising areas there.

A Mineral of the Future

Man has been familiar with sulphur since ancient times, as follows from the very origin of its name. In Old Russia, the word "sera" was taken to mean various combustible and smelly substances, resin and excrement. It appears that this word was derived from the Sanskrit word "sira" meaning "light-yellow". The old Russian word for sulphur was "zhupel" (combustible sulphur), which means not only combustibility but also "smelly". The chemical symbol S is taken from Latin "sulphur". This name seems to have been given by Greeks.

Sulphur was the only metalloid widely known in ancient times merely because of its native form. Since all considerable sulphur bodies were discovered on Sicily, it were ancient Greeks and Romans that got first knowledge of it. Egyptians used sulphur to produce paints and various cosmetic stuffs, and to bleach fabrics as early as two thousand years B.C. Sulphur was burnt in Ancient Greece to disinfect air and things in premises. Thus Homer writes in the "Odyssey" that, having got rid of all the pretenders to Penelope, Ulysses lit sulphur, spreading smoke throughout the home for "cleaning". It is noted in the Egyptian papyruses found in 1872 (they appear to have been written in the second millennium B.C.) that Egyptians regarded sulphur as a remedy from diseases. Assyrians applied sulphur against unconsciousness, sunstroke and skin diseases, and against insects.

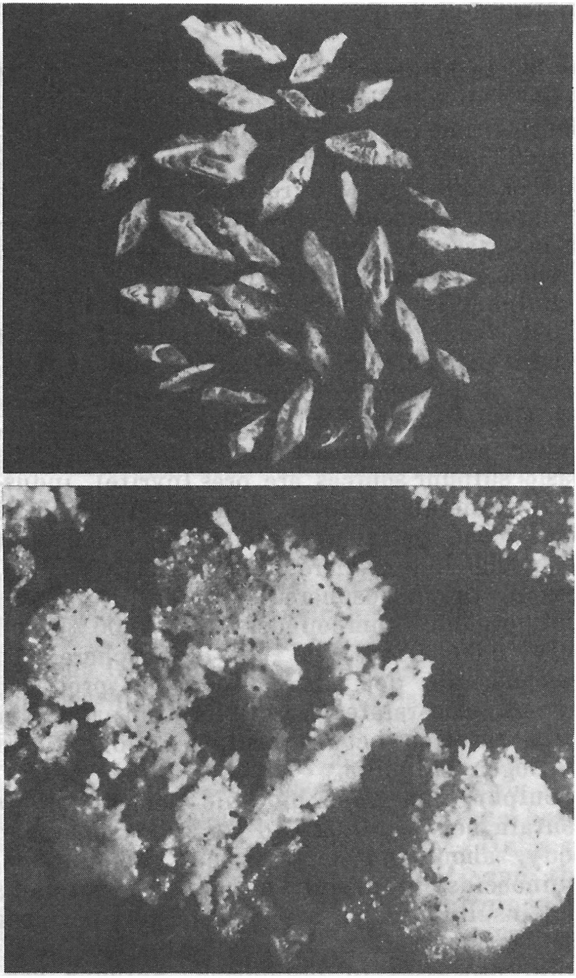
Because sulphur can burn, with the formation of a choke-gas, ancient peoples took it as the principal element of the Earth. Eruption of volcanoes and volcanic gas emission were treated as an action of the god Vulcan. Ancient Greeks regarded sulphur as the most combustible material; they called it "tayon", meaning divine, heavenly.

In the Middle Ages, alchemists believed that sulphur is condensed matter giving rise to fire. They regarded it as one of the basic sources of Nature—combustibility. Its easy inflammability and pungent smell, and the choke-damp property of its burning products gave an idea of a mysterious force concealed in this material and of its possibly supernatural origin.

In the 16th-17th centuries, sulphur was taken to be bitumen or fat earth containing fat acid. The physicochemical properties of sulphur became no more puzzling in the 18th century. The French chemist A. Lavoisier was one of the first who referred to sulphur as a natural element. Subsequently, this postulation was scientifically substantiated by the French chemist J. Gay-Lussac.

Sulphur is a widely distributed element on Earth, and its reserves are rather large. It occurs in nature both as native and as inorganic and organic compounds with nearly all the elements of the Mendeleyev Table, except gold, platinum and noble gases. The basic sulphur sources are ores (pyrite), industrial minerals (gypsum, anhydrite) and fossil fuels (coal, petroleum, oil shale). Much of it is in the hydrosphere (0.09%, 12×10^{14} t), less in the lithosphere (sulphides, sulphates and organic compounds, 0.047-0.06%), and only 0.0000025% in the atmosphere. In volcanogenic deposits, sulphur is produced by eruption-related reactions, in particular by a reaction between sulphur dioxide and hydrogen sulphide.

Sulphur is a major biogenic element: plants contain between 0.02 and 1.8% S and human body, about 0.4%. It is part of proteins, aminoacids, ferments, hormones, vitamins and insulin, which are of utmost importance for the structure of living matter and metabolic processes in organisms. Sulphur content is highest in the proteins of hair and horns. As part of other materials it is con-



Skeletal crystals of volcanogenic sulphur tained in nervous tissue, cartilage, bone and bile. When its content is too low, bones break up and hair comes out. Sulphur is of vital importance in diet. Pea, lens, oats and eggs are especially rich in it.

Sulphur is in the sixth group of the Mendeleyev Table. It is a single-component system with polymorphic transformations. Polymorphism is the capability of a solid with a certain chemical structure to exist in several crystal forms. Many crystals show this property. A substance can be a solid, liquid or gas depending on temperature and pressure; any crystalline body can likewise take this or that form. In other words, any crystalline phase is stable in a definite temperature and pressure interval, otherwise it undergoes transformation.

Sulphur is known to have three polymorphic modifications of which only the orthorhombic α-sulphur is stable in nature. It occurs as varying crystals and their intergrowths coloured in yellow tinges, and also as shapeless compact or earthy masses. At an atmospheric pressure and 95.5 °C, the α-sulphur is converted to a monoclinic β-sulphur. The orthorhombic sulphur crystals then become fractured, sometimes even powdery, and the ultimate particles already have the properties of a monoclinic sulphur. The conversion of the β-sulphur back to the α-sulphur is also accompanied by a clearly heard crackle. The process takes some time, rather than being instantaneous. The crystals are no more transparent in some time. Although their external form remains unchanged, their structure is actually that of orthorhombic sulphur.

The third modification, γ-sulphur, is also monoclinic; it is unstable at atmospheric pressure and common temperature. About 20 sulphur modifications can be obtained in the laboratory at different temperatures and pressures.

The orthorhombic sulphur has many (128) atoms in its unit cell. Lying at the base of structure are 8-member zigzag rings—closely connected S_8 molecules. Sulphur melts at 119 °C to form a transparent liquid, but with further heating to 200 °C, the liquid becomes red and very viscous. This is because the initially torn-up rings are then connected at their ruptures by their active ends. The result is a tangle of irregularly shaped chains. The restructuring is accompanied by heat absorption; hence, the proportion of chain structures increases with temperature.

Native sulphur is today a major element and mineral—it plays a large role in science and engineering. The "length of service" of sulphuric acid is in the region of 1 000 years; it was obtained by calcination of alum and green vitriol. Sulphur is considered to be a pusher of chemical industry. It is mostly used to produce sulphuric acid, fungicides and insecticides. Rubber is no more sticky but becomes more elastic when heated with sulphur (vulcanization). Addition of 1.5% of sulphur produces soft rubber for tyres. But if the rubber is volcanized with 30% sulphur, ebonite (hard rubber) is obtained.

Rubber elasticity was a mysterious phenomenon. Why is rubber elastic? When it is vulcanized with sulphur, the macromolecular chains are connected with each other by way of disulphide bridges formed by sulphur attachment to rubber matter.

Sulphur can be a superconductor. This has been proved by the scientists of the Institute of High Pressure Physics, USSR Academy of Sciences. They have run a unique experiment. A bar of common yellow sulphur was placed under a small press that actually bathed in liquid nitrogen at minus 243 °C. When the pressure rose to 500 thousand atmospheres, the bar began to conduct electric current without any loss.

Sulphur is used to bleach a cellulose paste in the paper-making industry, to produce paints, celluloid, matches and Bengal light, and to refine petrol; sulphuric acid is necessary for manufacturing blue vitriol, alum, soda, glass, bromium, iodine and other products. Sulphur is part of various chemical and pharmaceutical preparations and mineral pigments. In obtaining some synthetic materials, it is added to make them elastic. Much sulphur is utilized in agriculture, particularly in viniculture. American researchers have found that if even less than 1% S is added to the food of sheep, its wool becomes of a better quality.

Sulphur also has a number of other valuable properties: it is water insoluble, conducts electricity but slightly, and so on. Diverse building constructions can be made of sulphur with the help of a small cement mixer, gas burner and wood forms. Sulphur cement resistant to acids and caustics is obtained from a mixture of sand and sulphur. Hence it can be used to manufacture water and sewage pipes. Buildings made of traditional materials—sun-baked brick, clay and reed—become stronger and more resistant, especially in desert, if treated with a sulphur cement. Pulverized sulphur can be applied to the porous material of walls. The resulting coating rivals other coatings and paints: it is water resistant and elastic.

Canadian scientists offer making a mixture of 70% sand and 30% pure sulphur and then heating it to 120 °C to produce very strong brick blocks and even panels. They equal concrete in cost and durability. The recently obtained sulphur concrete, composed of thermoplastic sulphur and inorganic additives, is now under thorough test. Cement-sulphur mixtures, and an acid-proof mixture of sulphur, lime and sand are put into construction practice. Philippine engineers have obtained a new strong, watertight insulator by using sulphur instead of cement. Finally, sulphur foam plastic has been manufactured in Canada and used to advantage in laying pipelines and in road construction.

Highly promising is sulphur application instead of asphalt, for which aim placticized sulphur is used. This material is less energy consuming than Portland cement.

Modified sulphur can be utilized as part of materials for marking streets, parking lots and air fields. Also, the chemistry of sulphur organic derivatives is in the early stages of development.

Overall, there has been a short supply of sulphur in the world until very recently. In particular, this is true of the modern chemical industry. But there is now every ground to believe that mass production of sulphur is in the offing. It will be produced by purification units installed at thermal power stations, chemical plants and integrated metallurgical works. We refer to industrial smoke that carries much hydrogen sulphide and sulphur dioxide. This valuable raw material is not only lost irrevocably to the air but is also detrimental to everyone's health.

Much work in this field has been done at several plants in the German Democratic Republic. They have developed the technology and equipment for obtaining pure sulphur from process gas. Some of the hydrogen sulphide is burned in a special unit to produce sulphur dioxide. Then the hydrogen sulphide-sulphur dioxide reaction mixture is converted to elemental sulphur and steam (depending on the amount of hydrocarbons in the initial gas, the sulphur purity varies between 98 and 99.98%). This is the way in which sulphur is obtained and, at the same time, air is almost wholly cleared of contaminants. Such purification units already work at the Otto Grotewohl works in Belen and at the petroleum refinery in Schwedt an der Oder.

Quite dangerous is also the sulphur released from the Earth's interior during volcanic eruptions. Much sulphurous anhydrite escaped from Vesuvius crater and killed all living creatures in Pompeii and Herculaneum before they were buried beneath stones and ashes in 79 A.D.

Highly perilous is sulphuric acid that forms when rain water moistens volcanic products. Thus on the eleventh of February, 1979, the second day after Ambrim Volcano (New Hebrides, Pacific Ocean) woke up, nearly the whole vegetation in the southwestern part of the island was lost over an area of 90 km^2, many drinking water springs were poisoned, and many settlers suffered from skin burns. The cause was sulphuric acid, which also burned out some pastures located along the coast and greatly damaged cocoa and cocos palm plantations.

Sulphur can ignite in open-pit mines. Exploitation of sulphur deposits has shown that if the oxygen is in sufficient amount and temperature is high enough, ignition may occur even if the ore contains merely 10-12% S. At the same time, the content of sulphur in some ores is as high as 30-40%. Blast operations in an open-pit mine produce much finely dispersed sulphur dust. Explosive decomposition and the related temperature rise provoke sulphur ignition, with a subsequent rapid fire distribution throughout the sulphur dust-saturated space. The result is a flare that causes the sulphur ore to catch fire.

And now we revert to the poisonous sulphur that is thrown into the atmosphere by many industrial facilities, mainly by those which use hard and liquid fuels. (Among sulphur compounds, the atmosphere receives 95% of sulphur dioxide, 4.28% of hydrogen sulphide, and less than 1% of carbon disulphide and other compounds.) Sulphurous anhydrite is oxidized in the air to sulphuric anhydrite, which reacts with water vapour to produce sulphuric acid. Because of this, the water of clouds and fog can be extremely acid, its pH being frequently as low as 2.5 or even lower. The acidity of a medium (as a rule, this is a water solution) depends on the presence of free hydrogen ions, H^+. The concentration of these ions is designated by symbol pH—the negative $\log_{10}$ of hydrogen-ion activity in solution (mole/l). Thus the pH of chemically pure water is 7 at 20 °C. Solutions with pH less than 7 are called acidic, while those with pH equal to 7 or more, alkaline.

Acid atmospheric precipitation is detrimental to man, animals and plants, and intensifies corrosion of materials and constructions. It is also highly dangerous to ancient monuments. Tiny amounts of hydrogen sulphide are enough to bleach any surface coated with a lead-bearing paint.

As a whole, vegetation is more sensitive to the presence of sulphurous dioxide in the air than man. Conifers are most sensitive in this respect. This is because of the gypsum crystals that grow in the stomas of pine needles when the sulphuric acid falling from the sky reacts with the calcium salts that the pine exudes to neutralize the acid. The gypsum crystals plug the stomas, and the tree may perish from suffocation.

We still know but little of the fate of sulphur in the environment, of the sulphur exchange in nature. The end-product of such an exchange is considered to be gypsum alone. But what about other minerals as end-products? Different plants differently absorb sulphurous anhydrite and then transform it into sulphate. It is well known that foliage trees react on sulphur compounds by forming not only sulphate but also poisonous carbon disulphide. Also, the gas methane is abundant in the Earth's atmosphere, and its concentration has been growing rapidly in recent years (1.3% a year, on average). This gas absorbs the infrared radiation from the Earth's surface, which, in its turn, enhances the so-called greenhouse effect. Undoubtedly, this gas also participates in mineral formation.

The only place on the Earth where large amounts of native sulphur were mined for many centuries was Sicily Island, part of the Naples Kingdom. The island was frequently the object of rows and even wars. England was especially sensitive to the Sicilian sulphur monopoly. To conquer these sulphur deposits, English fregates repeatedly bombarded the shores of Sicily. English industrialists soon held grip over the sulphur production on this island; they made fabulous profits from Sicilian sulphur during several decades.

After Swedes developed a cheep method of obtaining sulphur and sulphuric acid from pyrite, the envious European countries directed their interest towards Spain, where extremely rich pyrites bodies had been discovered. But sulphur has never been extracted from the pyrites in commercial amounts.

This situation lasted until the turn of the 20th century, although considerable native sulphur masses were discovered at depths from 150 to 200 m in Louisiana and Texas, USA, as early as the second half of the 19th century. The rock there contained 75-80% S, but numerous attempts to mine sulphur from these depths were unsuccessful. Shaft sinking was ceased because much hydrogen sulphide began to escape from the Earth's interior at a depth of 30 m. The years passed, but sulphur still lay buried. And it would have lain there for many more decades if it were not for the American engineer Herman Frasch. He arrived at the idea of melting sulphur at depth and transporting it to the surface in a liquid state, that is without shaft sinking.

Not everybody knows, however, that the fundamentals of this technique were developed in Russia by the amateur chemist K. Patkanov as early as 1883. Chemistry was his beloved subject even when he studied at the Agricultural Institute. Wherever he pursued his career after graduation, K. Patkanov invariably ran simple experiments in his small chemical laboratory. While a forest inspector in the Northern Caucasus Mountains, K. Patkanov took interest in native sulphur. It is quite possible that he had some knowledge of deposits in Dagestan. But, as a matter of fact, he closely studied the sulphur from the Kara Kum Desert. A big piece of ore from the Kirkh-Chulba region was presented to him by his colleagues. The researcher dissolved a small chunk of sulphur ore in heated sulphuric acid.

As a result, "the ore gave off sulphur, which, on getting together to produce a mass, became to float like yolk surrounded by sand and small gypsum crystals". Siliceous particles settled down on the bottom of the vessel. K. Patkanov poured off sulphuric acid and then took out from the vessel a lump of pure sulphur without any siliceous particle stuck to it.

After experimenting on other sulphur ores, the researcher decided to use common hot water to extract sulphur from the rock. The experiments in this direction were continued in the laboratories of Moscow University and Forestry Institute. The following conclusion was made: "... on melting in water heated under pressure to a certain temperature, the sulphur in a sulphur ore separates from the enclosing rock and solidifies but without combining any more again with the rock as soon as this rock is moistened with water". K. Patkanov not only proved a possibility for sulphur to be melted out by means of water heated under pressure to the temperature above the melting point of sulphur but also designed a small device for the purpose.

At the same time Herman Frasch hired workers to drill a borehole to the base of the sulphur-bearing bed in one of the salt-dome deposits in Louisiana. Three concentrically arranged pipes were sunk into the hole. H. Frasch decided to pump water heated to 170 °C down the annular space between the middle and the inner pipe. He believed that the molten sulphur must have been forced up through the thinnest inner pipe.

These were expectations, and many did not believe in them. One of the rabid opponents of the method, a famous authority in technological processes, even said in the heat on the debate that he was ready to "eat up each ounce of sulphur that would be pumped out on the surface". But H. Frasch believed in his expectations and got his way. A spout of golden-brown sulphur first stroke from earth in 1891, and 40 barrels were filled in 15 minutes and the sulphur went on to pour out.

K. Patkanov wrote in one of the issues of *Gornyi zhurnal* (*Journal of Mining*) in 1897 that he was in a hurry to claim a discovery, "with the sincere desire that it should be published in Russia before it appears in some specialized foreign publication". But this information was clearly too late. The world literature refers to H. Frasch, rather than to our compatriot K. Patkanov, when the method of underground sulphur melting (USM) is mentioned.

The USM method is based on the low melting point (112-119 °C) of native sulphur, its high density (1800 kg/m^3) and low viscosity at 120-150 °C. Its essence consists in sulphur melting by a heat carrier (water at 165 °C) directly in the orebody and pumping it out on the surface through boreholes. This method is advantageous as compared with open-pit and underground mining methods in that it allows sulphur extraction from depths (approx. 800 m) too great for any other methods known for today. Moreover, the sulphur, extracted by the way of underground melting, is extremely pure and very cheap.

Cryptocrystalline Sulphur

Most deposits of sulphur contain its cryptocrystalline variety. Although it has repeatedly been mentioned in literature, many aspects of its nature remain unknown. The mode of origin of cryptocrystalline sulphur was but very little studied. In some mineral deposits, it constitutes bulk of commercial ores.

The cryptocrystalline sulphur is quite unlike the crystalline sulphur. It is a relatively compact uniform mass coloured in different tinges of brown, with a dull or waxy lustre and an irregular to subconchoidal fracture. An idea on the appearance and size of the particles of cryptocrystalline sulphur can be obtained from electro-microscope images at X10 000-15 000. In the sulphur-bearing clay from the Ciscarpathians, the particles of cryptocrystalline sulphur are ellipsoidal, rounded or irregular in shape. The irregularly shaped particles predominate; they are frequently combined into accumulations of three to four individuals. These particles are at least 0.06 μm in size, whereas the rounded ones are as large as 0.9 μm, atfracting, so to say, irregular, elongate sulphur particles. The ellipsoidal particles are clearly distinguished by their size (up to 1.4 μm) and shape against the background of finer sulphur. On destruction, the cryptocrystalline sulphur of the Ciscarpathians is divided into 1-2.5 μm particles. These are rhombic, somewhat elongated, with sulphur-inherent lamella terminations.

The particles of finely dispersed sulphur, which approach in size to those of the cryptocrystalline sulphur, are structurally specific. In the sulphur deposits of the Surkhandar'ya depression, the fine-dispersed sulphur occurs either along cleavage joints cutting through gypsum or forms a thick dissemination in it. Under the electron microscope, such sulphur is distinctly dendritic, its particles being about 10 µm in size. The dendrites (from Greek, *dendron*, a tree) arise where the inflow of the feeder to a growing crystal is insufficient. This crystal does not expect, as it were, a supply of large masses of material; it has, so to say, to seek food for itself, so it grows away from the crystallization centre. At their ends, the branches of dendrites are bounded by faces inherent in the orthorhombic sulphur.

The slowing down effect of impurities greatly favours the generation of sulphur dendrites. It was noted long ago that under the same conditions the dendrites grow in contaminated environments, whereas the common, wholly defined crystals, in pure ones. A growing crystal takes a pure material from the solution, and the remaining contaminants accumulate nearby and hamper the face growth. While growing, the crystal forces its way between such particles to become arborescent. The more abundant the contaminating particles along the way of its growth, the greater is the branching. The cryptocrystalline sulphur always contains clay impurities. So it is these that probably make harder the growth of sulphur aggregates.

The above data confirm the diversity of microscopic sulphur segregations; it appears that their origins are different.

In the Shorsu and Changyrtash deposits, Surkhandar'ya depression, the cryptocrystalline sulphur fills tectonic fissures with the formation of thin veinlets, or occurs as crusts on the walls of cavities. This variety is observed at the Gaurdakskoe deposit as varied disseminations ranging from fine, rounded grains to coarse, elongated ones of intricate outlines. The sulphur frequently intrudes a fine-grained carbonate mass, filling pores and interstices between fine calcite grains.

Diverse are the cryptocrystalline sulphur segregations in the Ciscarpathians. Veinlets, fine and dense disseminations, and lense- and petal-shaped concentrations predominate in the clay. Both isolated grains and a thick network of cutting and connecting veinlets occur in the limestone. The large segregations have more distinct contacts with the enclosing pelitomorphic limestone than the small ones. With the decreasing size of inclusions, the sulphur seems to become more and more dispersed; its relationships with the pelitomorphic limestone become more complex. The sulphur and calcite grow one into another, as it were.

The cryptocrystalline sulphur of the Ciscarpathians contains silicon, aluminium, magnesium, calcium, iron, manganese, titanium, molybdenum, copper, sodium, potassium, strontium, barium, arsenic, lead and selenium. And the following minerals were found in it after it had been dissolved in carbon disulphide: gypsum, plagioclase, quartz, amphibole, glauconite, volcanic glass, calcite, clay and organic matter. The hardness of sulphur is 15.31-19.36 kg/mm^2 and density 2.04 g/cm^3.

In the Vodinskoe deposit, the cryptocrystalline sulphur occurs in all sulphur-bearing beds as small (1-2 cm) inclusions. More often than not, it is present at the margins of sulphur-calcite concretions. A concretion is a rather compact, relatively homogeneous fine-grained body coloured dark brown, at places greenish, with an uneven fracture and a dull lustre; it comprises particles about 0.008 mm in size. The cryptocrystalline sulphur clearly replaces gypsum in the cavities of sulphur-calcite concretions. In some concretions, this variety is confined to free space between well-bounded sulphur crystals, as well as to pores and fractures in the rock. In the mineral deposits discovered in the middle reaches of the Volga River, the sulphur was definitely derived from direct precipitation from sulphur-bearing solutions, and from gypsum replacement.

The mode of origin of the cryptocrystalline sulphur remains unclear in many respects. Why did it precipitate in a polycrystalline form in some cases and as well-developed crystals in others? One of the causes appears to be the different states of the sulphur-bearing solution, in particular the different degrees of its supersaturation which, in turn, was governed by the oxygen content of the solution. Few relatively large crystals formed with a slight supersaturation and at a low crystallization rate. But the number of seeds grew appreciably with a moderate supersaturation and at an insignificant crystallization rate. In these cases, the coarse-crystalline sulphur was followed by crystalline-granular sulphur with less perfect faces. The strong supersaturation favoured the precipitation of cryptocrystalline or colloidal sulphur.

The occurrence of cryptocrystalline sulphur in the form of a relatively well-bounded crystal is mysterious. The sulphur was found at the centre of a limestone-sulphur concretion (the Vodinskoe sulphur deposit). The "polyhedron" is enclosed in crystalline-granular sulphur, but is immediately surrounded by fine-grained gypsum with sooty iron sulphide inclusions.

The cryptocrystalline and crystalline-granular varieties have a "crystal-in-crystal" structure in which the inner crystal differs in colour and physical properties from the surrounding sulphur aggregate.

The polyhedron is elongated along the *c*-axis, being 2.8 cm in this direction. It has four simple forms, most common for sulphur. All faces are covered with winding striations that to some extent resemble the tracery on the finger's inner surface.

The polyhedron is made up of a chocolate-grey brown compact material. Recrystallized parts, even small (up to 0.1 mm) well-defined crystals of yellow sulphur are well seen. Identical areas of unevenly recrystallized sulphur are observed in a thin section prepared from part of the crystal. Tiny (0.008 mm) sulphur particles are combined into a dark-coloured fine-grained material that on microscope stage rotation does not change its colouration in a polarized light. The closely contacting grains are generally irregular; more seldom, their boundaries are rectilinear. The grains larger than 0.01 mm tend to become rhombic. The chocolate-grey brown material is contaminated with irregular quartz grains, as large as 0.2 mm, with their inherent wavy extinction. Smaller quartz grains occur in the insoluble residuum of cryptocrystalline sulphur from the Ciscarpathians. No quartz has ever been found in the crystals of light-yellow recrystallized sulphur.

X-ray data indicate a somewhat worse symmetry of the cryptocrystalline sulphur than that of the well-crystallized sulphur. Some reflections on the diffraction patterns for the former show a clear split into two lines. The greatest split is observed on the diffraction patterns for the Vodinskoe cryptocrystalline sulphur.

Unlike the Ciscarpathians, where the cryptocrystalline sulphur is an older generation, at the Middle Volga deposits it is younger than the coarse-crystalline sulphur. In sulphur-calcite concretions, the cryptocrystalline native sulphur precipitated in the interstices between light-yellow sulphur crystals. The cryptocrystalline sulphur segregation itself is the cast, as it were, of a cavity between the earlier formed striated sulphur crystals.

Coarse-Crystalline Sulphur

Sulphur crystals occur in different shapes.

Crystal habit. The sulphur habit is defined on the basis of predominating faces of this or that simple form. Dipyramidal, prismatic, pinacoidal and pseudotetrahedral habits are characteristic of sulphur crystals. The types of habit are determined from the relative development of crystals along three crystallographic axes: [100], [010] and [001]. Three habit types are hence distinguished: elongate, isometric and flattened. The simple forms grow unequally in them. As the growth along the third axis [001] is slowing down, the elongate crystals are transformed into flattened ones.

The crystals elongated along [001] and roughly isometric ones of a dipyramidal habit are common in most of the sulphur deposits. Thus 53% of crystals in the Ciscarpathians are elongated, while the number of those flattened along [001] is about half the isometric ones. At the Shorsu deposit, 38% of crystals are elongated, 46% isometric, 14% tabular and 2% rod-like. N. Yushkin described peculiar pseudotetrahedral crystals at the same deposit.

The sulphur crystals in the salt differ in habit from those in the caprocks at salt domes within the Dnieper-Donets depression. The salt contains elongate (50.5%) and flattened (49.5%) dipyramidal and pinacoidal crystals, and caprocks, elongated (70.5%) and isometric (29.5%) dipyramidal crystals.

Both elongate and isometric crystals occur in coal seams. The former predominate (75%); they have a dipyramidal habit. In sulphide deposits, all crystals are elongated, and have a dipyramidal habit.

All this shows that sulphur crystals are anisotropic as to their growth rates. Both the external and internal morphology of crystals are due to their structure and the environment. If the structure exerts a greater influence and the bonds in the crystals are stronger, common sulphur crystals grow up with well-developed dipyramidal faces. If the bonds in the crystal and environment are nearly the same, the environment starts to predominate.

Sulphur typomorphism. Sulphur crystals have different typomorphic properties in different mineral deposits.

Two crystal types have been distinguished on the basis of the diversity of simple forms delineating the crystal. The first type is variable in outer appearance but its range of simple forms is relatively narrow. Such crystals were found in the sulphate-carbonate rocks of commercial sulphur bodies and in the oxidation zone of sulphide deposits. The crystals are elongated, isometric, tabular, or lamellar. The number of simple forms does not exceed six for the sulphur from the Ciscarpathians and Poland; four, the middle reaches of the Volga River; seven, Soviet Central Asia; four, the Kerch Peninsula; and five, the oxidation zone of sulphide deposits. The same is true of the sulphur twins found in the deposits of the Ciscarpathians, Poland and Soviet Central Asia.

The second crystal type is characteristic of the salt domes in the Dnieper-Donets depression, a deposit in Syria, volcanogenic sulphur deposits in the Kuril-Kamchatka volcanic arc, and coal seams. The sulphur crystals from these regions display from 10 to 16 simple forms.

The appearance of different simple forms on sulphur crystals can be explained with the help of the Curie-Gibbs-Wulff principle based on a notion of the surface energy of a crystal. A change in the physicochemical state of the solution affects not only the surface energy of the whole crystal but also the specific free surface energy of each simple form. Moreover, the energy of a particular simple form varies while the form grows. Thus the plane (111) of diamond has the least surface energy. That is why the preferential appearance of the octahedral form at the time of origin and initial diamond growth is quite normal. The plane (111) of sulphur has the least specific surface energy. It is invariably found on sulphur seeds. But as the sulphur crystal is growing, other planes may become prominent.

Why does the specific surface energy of the faces of simple forms vary, thus provoking changes in crystal faces? According to N. Yushkin, this depends on two factors: the presence of a solvation sheath on crystal faces and of surface-active organic substances in sulphur-settling solutions. We further elaborate on the subject.

The solvate sheaths on sulphur crystals can be either anionic or cationic. Interestingly, simple form-rich sulphur crystals nearly always form in a chlorine-bearing environment. Such crystals were, for instance, found in salt domes and rock salt units, as well as just on volcanoes. And we know that the volcanic gases are rich in chlorine—one of the elements present in magma.

The second anion that affects the specific surface energy of faces is HSO_4^-—a product of sulphuric acid dissociation at sulphur deposits in areas of an arid climate. Thus 14 simple forms have been found on the sulphur crystals from the Al Shaheri deposit.

The surface-active organic substances hamper the growth of the dipyramidal habitual face. So the crystals possess a dipyramidal habit.

Sulphur regeneration. Like some living things—sea star, lizard—many crystals can restore their broken-off parts. This wonderful phenomenon in the realm of minerals is called regeneration. The notion of a "regenerated" ore deposit was formulated by the geologist G. Schneiderhen in the early 1950s. This phenomenon is best manifested on the polyhedra of the Shorsu and Ciscarpathian sulphur. You can observe at the Shorsu deposit that the rounded edges of yellow sulphur crystals are covered with bright faces of brownish-yellow and brown sulphur. Small well-defined crystals arise on the edges and faces of the earlier formed crystal. The regeneration probably takes place when the sulphur-undersaturated mineral-forming solution later becomes a sulphur-supersaturated one. The faces of partly dissolved sulphur crystals from the Ciscarpathian deposits are regenerated (heeled up) by lemon-yellow to light-yellow to almost colourless finely crystalline sulphur. This phenomenon is especially prominent where a sulphur crystal has its apex slightly dissolved. The origin and growth of new crystals of sulphur are in full agreement with the crystallographic orientation of the parent crystal. The planes and edges remain all the time straight and distinct. Such a crystal differs in outer appearance from the surrounding sulphur polyhedra in that it is dichromatic.

The regeneration of brown sulphur polyhedra with the formation of an aggregate of small dipyramidal crystals is less common. Though parallel to the main crystal, they extent beyond its boundaries. This is the way of generation of sceptre-like sulphur crystals resembling an intergrowth of two polyhedra.

The regeneration of native sulphur crystals can be considered in a broader sense, with reference to the entire sulphur deposit. The point is that at some deposits in Soviet Central Asia and Dagestan, and at the occurrences in the Kerch Peninsula (Gornostaevka, Chokrak), the sulphur content of oxidized ores, including their contact with the unaltered rocks, is much higher not only than that of the upper part of the oxidation zone but also of the unaltered sulphurated rock. Thus, the unaltered ores from the Syrian deposit generally contain not more than 17% S, while the oxidized ores 45-46% S—an apparent concentration of native sulphur in the oxidation zone of this deposit.

The sulphur crystals from this part of the orebody are quite fresh and are unusually associated with the typical minerals of the oxidation zone (alunite, halotrichite, copiapite, gypsum). The sulphur distinctly replaces the gypsum derived from sulphur oxidation; it settles in interstices between the minerals of the oxidation zone, fills pores and cracks in the minerals. All this is enough to suggest that the sulphur has been formed in the orebody quite recently.

As in the unaltered sulphur ores, the fine-grained sulphur recrystallizes and becomes coarse-grained because it can easily be redistributed in the newly formed ores. The front of secondary sulphur mineralization advances gradually to include the lower and middle parts of the oxidation zone but never comes to the surface. The thickness of the regenerated part of the sulphur deposit is directly proportional to that of the oxidation zone. The newly formed ores contain no calcite.

In the Gaurdakskoe deposit, the regenerated portion of the sulphur body lies low in the oxidation zone. The sulphur is generally radial-fibrous and is associated with gypsum and anhydrite derived from gypsum dehydration.

Another example of the regeneration of a sulphur deposit is afforded by the Giik-Salgan orebody (North Dagestan). The deposit has been known since long ago. By 1917, several *hundred thousand poods** of sulphur had been extracted from it. The surrounding light-grey limestone is exposed in the side of the Giik-Salgan Gourge, roughly 300 m above its bottom. Ore relics have been found in a cave extending 15 m inside the ridge. It is possibly an opening through which sulphur ores were mined. A strong hydrogen sulphide odour is felt in this cave, so it is dangerous to stay there.

Native sulphur concentrates near the surface of the limestone weathered to a sulphur-gypsum rock. So gypsum is the main component of the ore. The sulphur is associated with gypsum and anhydrite, which is a product of gypsum alteration in an acid environment. The ore contains up to 26% S.

In the Gornostaevskoe occurrence, the sulphur lies low in the oxidation zone of the Sarmatian limestone weathered to a friable sulphur-gypsum material. The rock contains 13% sulphur. In the Chokrakskoe sulphur

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* A pood is 16.38 kg.— *Translator's note.*

occurrence, the regenerated portion of the orebody is enclosed in Quaternary deposits. The sulphur content of the orebody is as high as 15%.

At the Gaurdakskoe deposit, the elongate sulphur crystals predominate, while the isometric and tabular polyhedra are approximately distributed in the same way. The dipyramidal crystals are more widespread. The prismatic and pinacoidal crystals are nearly equal in distribution frequency. At the Syrian deposit, the isometric crystals are less common than flattened (tabular and lamellar). About half of the crystals found are dipyramidal.

The volcanogenic sulphur crystals from the Kuril-Kamchatka volcanic arc is elongated nearly exclusively along [001] and has a dipyramidal habit. The number of simple forms bounding them is equal to their number for the crystals from the regenerated portions of sulphur deposits and is less than for the crystals from salt domes.

The above features of volcanogenic sulphur are due to the thermodynamics of its crystallization. The distinctions between the habits of sulphur from the sulphate-carbonate rocks were mainly caused by changes in the amounts and compositions of the surface-active materials (oil and its derivatives) that are present in the mineral-forming solutions and affect the specific surface energy of growing crystal faces. The degree of mineralizer's supersaturation exerts a certain influence on the sulphur habit: to each supersaturation degree corresponds a certain shape of the sulphur crystal; the lower the degree, the greater is the amount of faces on the crystal.

Skeletal crystals. They may be referred to as puzzling. The point is that when the effect of the environment is such that the growth rate is sharply different in different directions, the crystalline matter fills, not the whole polyhedron but only some of its volume. This is the case where the amount of the mineral-forming material is insufficient for a normal crystal to form.

At some deposits, for instance at Shorsu, skeletal polyhedra prevail over other kinds of sulphur crystals. Terminology, geometry, symmetry and modes of origin of skeletal crystals are dealt with some works of the Soviet authors. According to these authors' classification, this type falls in the internal and external classes of the three-dimensional space group. Both consist of simple and complex skeletal forms.

The internal class predominates among skeletal sulphur crystals. It is chiefly composed of imperfect crystals the faces of which are covered with variously shaped hollows. These are triangular in the sulphur crystals from the Ciscarpathians, owing to an insufficient inflow of the mineral-forming material to the polyhedron. You should take into account that if the material comes with difficulty but steady from the crystal edges, triangular or trapezoidal hollows form at the face centre.

If the inflow is unsteady, asymmetric hollows appear, which are shifted to one of the face edges. More frequently, several growth hollows are arranged in chain, rather than being solitary, to produce a pattern on the bright surface of the face. The crystals with a block-mosaic structure of their faces stand apart to some extent, but they also result from skeletal crystallization.

When the skeletal growth occurs on the crystal faces of the Gaurdakskoe sulphur, these become stepped, perforated and cavernous, serrated in outline. Crystals were noted with stepped hollows, the steps conically converging to the bottom like staircases. More often, only several faces of a crystal are skeletal. Some hollows look like rain rills extending across the whole crystal. When such crystals intergrow, intricate dendritic forms are generated.

Skeletal features are frequent among volcanogenic sulphur crystals. No faces as is usually understood are present on them; their locations are occupied by funnel-like hollows built up of numerous overlapping triangular frames. These differ in width, so the funnel sides look stratified. Some crystals consist solely of edges. If the younger, successively overlapping layers are wider than the older ones, they may close the hollow at the centre of the face.

The complex internal skeletal polyhedra are less common; they have been noted only for the sulphur from the Vodinskoe and Shorsu deposits. The interstices between the branches of a skeleton are filled with a later sulphur generation and bitumen.

The external skeletal crystals occur chiefly in the Shorsu and Ciscarpathian deposits. They look like boxes, cases, frames and apex features. The boxes were observed only at the Razdol'skoe deposit. These crystals are vacuous crystals of sulphur. The hole in the crystal is surrounded by a rim of serrated plates. The bottom of the hole is formed of calcite and sulphur. The depth to it from a barely noticeable alveole is up to 4 mm.

The cases—imperfect (ruptured) skeletons—were noted for volcanogenic sulphur. They do not differ at first glance from normal sulphur crystals. But if you examine the crystal more closely, you will notice a slot in one of its faces—the entrance into a large cavity at the centre of the crystal.

The frames are the result of a systematic overgrowth of small sulphur crystals on the edges of a large crystal. If these crystals cover all edges and are in close contact with one another, the frames are formed. Like the cases, they can be continuous or not. The most complete frames on the edges of sulphur crystals were observed at the Shorsu deposit.

The apex features are oriented overgrowths of small sulphur crystals on the apices of a larger crystal. They can be regarded as underdeveloped edge frames in which the sulphur of a younger generation has not filled the mid-point of edges.

The mechanism of formation of skeletal sulphur crystals is not wholly understood. In sulphur deposits surrounded by sedimentaries, such crystals are produced by crystallization from a viscous material, which hampers the inflow of feeders to the polyhedron.

What solutions did promote an increase in the viscosity of the mineral-forming material? Generally speaking, all sulphur deposits tend to occur in oil and gas regions. The hydrocarbons present in the sulphur deposits themselves directly prove an interrelation between oil and sulphur. Moreover, they participate in sulphur generation. They rise the viscosity of solutions, impair the release of crystallizing particles from the solution and complicate the motion of particles towards the crystal surface.

The above description shows that sulphur polyhedra differ in the character of skeletal crystallization.

If we assume that the sulphur crystal habit is a measure of the viscosity of mineralizers and, hence, of hydrocarbon participation in native sulphur precipitation, then the shape of sulphur polyhedra indicates to some extent the nature of the bituminous materials engaged in mineral formation.

The carbon of the calcite from limestones in sulphur deposits is genetically related to the carbon dioxide derived from gaseous hydrocarbon oxidation. No sulphur deposits known to date, except Ciscarpahtian and Sicilian ones, show such enrichment of the sulphur-related carbonates in the light isotope ^{12}C $(70^0/_{00})$ as compared with the sedimentary calcite. The habit of sulphur polyhedra was affected by methane, a chief constituent of sulphur-precipitating solutions. This refers, above all, to the origin of such skeletal sulphur crystals as boxes and those with bloc-mosaic faces.

The carbon of the calcite from the carbonates associated with sulphur in other deposits is genetically related to the carbon dioxide produced by oil oxidation. Naturally, the oil increased the viscosity of mineral-forming solutions to a greater extent than the gaseous hydrocarbons. Hence the skeletal sulphur formations from, say, the Central Asian deposits differs substantially from that of the Ciscarpathian ones. This situation at the Shorsu deposit may account for the overgrowth of small sulphur crystals on the apices and edges of large crystals. Oriented overgrowth is also characteristic of the sulphur from the Ciscarpathians, but no typical edge and apex forms have been found there.

From the above it can be concluded that the edges and apices of sulphur polyhedra have an enhanced energy only if the mineralizer is very viscous. In a less viscous environment, the crystals (more often lamellae) suspended in the solution stick to crystal faces, rather than to edges and apices.

The skeletal crystals from the volcanoes of the Kuril Islands are due to a considerable supercooling of the fluid escaping from deep in the Earth. Conditions for the skeletal growth of volcanogenic sulphur crystals appear to arise already when the concentration of sulphur in the fluid only slightly exceeds the saturation concentration for the edges and apices, and with rapid sublimation these can grow more intensely. The formation of composite skeletal crystals reflects the variability of crystallization conditions. At the beginning, the sulphur crystals grew obeying the greatest growth rate principle, with the prevalence of edge development. Such a growth is possible when the fluid supercools rapidly. Later, the sulphur crystals tended to acquire an equilibrium shape. Their origin required for the fluid to be less supersaturated and to cool slower than during the initial (skeletal) crystallization.

We discuss only one feature of skeletal crystallization, namely that related to the surface-active materials (oil and its derivatives) present in the mineral-forming solutions. The shape of skeletal sulphur crystals is indicative of the viscosity of the mineral-forming solutions. Skeletal volcanogenic sulphur crystals are generated when the fluid supercools deeply.

Twins. Twins are composite crystals of one mineral species, in which the individual parts are related to one another in a definite crystallographic manner. They are characteristic of some minerals, for instance cinnabar and plagioclases, but are sparse among sulphur crystals. In twins, the structures of crystal individuals are interrelated by the symmetry elements other than those of single crystals. These elements are called a twin axis and a twin plane. The unusual shape of twins is due to their peculiar symmetry. There occur growth twins, transformation twins and gliding twins. One and the same mineral can twin according to different laws. Seven of them are known for sulphur twins: (101), (110), (011), (111), (211), (511) and (901).

Twinning on (101) is most common. This means that the twin plane in this case is the prism face {101}. In sulphur-bearing rocks, these twins occur in cavities and relatively compact pelitomorphic limestone. Twins are divided into two types by the way they line cavities. Predominant are those lining small, roughly isometric voids in limestone. They look like small, freely growing needles. Other, mostly elongated voids are lined with twins attached by one of their ends to the bottom of the void and by the other to its ceiling or to any other crystal. As a rule, they are variably curvilinear and break up if you try to extract them.

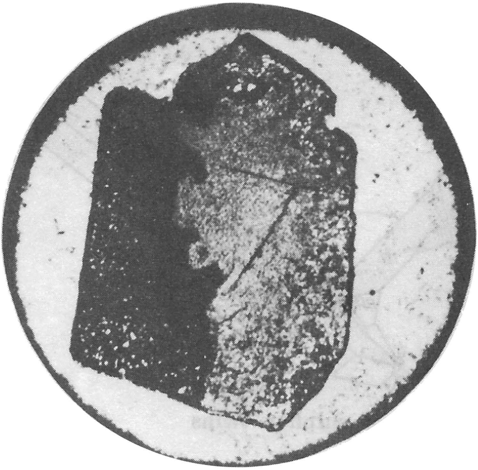
The twins occur as small four-faced prisms with interfacial angles equal to 106°25′ and 73°35′. They resemble single crystals in external form, all the more so that one individual is better developed than the other and the re-entrant angles between the faces of both individuals are noticeable only under large magnification.

The twinned structure of crystals is well seen under the microscope. It usually shows two parts that are elongated parallel to its largest dimension. When you rotate the stage of the microscope, you can see only one individual displaying a clear distinction at 23° to the central hair of the microscope. Only separate limited areas extinct in some cases; they occasionally have rectilinear boundaries with the non-extinct areas.

In the twins, each of the four faces of the dipyramid {111} belongs to two individuals. The remaining faces of both individuals are at the apex and form re-entrant angles between one another. The outer appearance of the twins is rather stable. It is nearly the same, with only slight variations, in different ore deposits. The twins are rhombic in plan.

No one can satisfactorily explain the occurrence of twins in relatively compact pelitomorphic limestone. Cryptocrystalline sulphur generally concentrates in such limestones. In the pelitomorphic carbonate mass, the sulphur twins on (101) occur as small (up to 2 mm) phenocrysts. Unlike the previously studied twins, both these individuals are developed well enough according to this law, and are separated by a winding composition face.

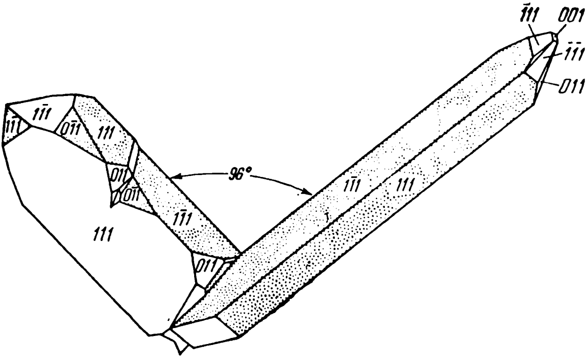
The twins on (110) are extremely scarce in sulphur ores. They look like common crystals, but the re-entrant angles between the least-developed faces confirm that they are doing twins. This is also found easily under the microscope—you can see irregular areas that extinct symmetrically to the twin elongation (along the *á*-axis). The extinction angle between these areas is equal to 78° (theoretical angle 78°14′); the twin plane is (110). The rod-like habit of twins is due to the well



A sulphur twin [illegible] ıtomorphic limestone

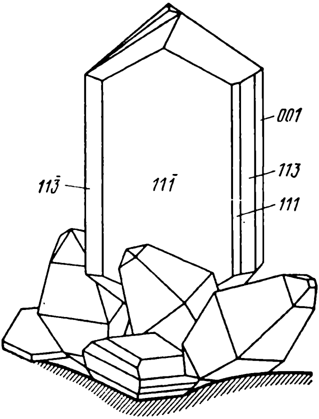
developed dipyramid faces {111} and {113}. The less developed faces of the same simple forms produce re-entrant angles at the apex of the twin. The pinacoidal face {001} is common to both crystal individuals, whose separation face is indistinct.

The twins on (011) are very scarce. Like the previous ones, they resemble single crystals very much, and only a close examination under the microscope has made it possible to find on them faces with re-entrant angles. The twin best shows dipyramids {111}, and there are always eight of them. Only two dipyramidal faces {111} are well developed in each individual. A combination of four such faces (two faces per each individual), together with the prism faces {011}, forms the rod-like habit of the twins. The remaining faces of both individuals are less developed; they occur at the apex and form a re-entrant angle between one another. The twin plane is (011).



An intergrowth of sulphur twins

The twins on (111) are sparse and have not been studied. The author of this book was lucky to find at the Rozdol'skoe deposit a single composite crystal developed according to this law. Unlike the above-described twins, it is simpler in outer appearance. Both individuals consist of simple forms common to sulphur crystals; their shape resembles that



A sulphur twin among common crystals

of nearby single crystals. One individual is larger than the other, which is more complex, their common dipyramidal plane being {111}. The latter is composed, so to say, of several parallel intergrowths.

The twins on (511) were found in the ores of one of the deposits in Syria. Each is made up of two well-developed individuals with the angular distances between the pinacoids {001} equal to 9°05′. Both individuals are best developed along the *c*-axis, being as long as 3 mm in this direction. Unlike the above-described twins, they consist of many faces, of which most developed were found to be the planes of prisms {101} and {011} and of a pinacoid {001}.

The twins on (901) were found together with those on (501) but are more common. Both individuals are so strongly interpenetrated that become very similar to the nearby sulphur crystals. But under the microscope, they display twice as many faces, which form re-entrant angles. Some re-entrant angles look like slight protrusions. The first (principal) individual is rather simple in shape; the second is included in the first as segments of different sizes. The faces of a prism, {101}, and pinacoid, {001}, are best developed.

Multiple twins. Besides the twins proper, there have been found regular multiple twins of eight individuals, with parallel faces, and casual ones. All of them were seen in the sulphur ores from the Ciscarpathian and Gaurdakskoe deposits.

The eightfold twins are due to a regular twin interpenetration on (101). Each twin is divided by a separation face into two sectors. These sectors extinct at 23° to the separation face, that is they behave under the microscope like the above-described twins on (101). The boundaries between the twins and individuals are clear cut and winding. The eightfold twin is rhombic in cross-section. Each of its sides is common to several individuals. Nearly all individuals contain the segments shared by the opposite individual of the twin.

Some twins on (110) and especially on (101) include elements of the parallel orientation of certain faces. These faces alternate in a step-like manner and gradually thin out toward the apex, which makes the twin to look like an obelisk.

Irregular twins are scarce. A twin on (101) grown by the face of a dipyramid {111} together with the face of a prism of a twin on (110) at 96° has been found at the Rozdol'skoe deposit.

At the Gaurdakskoe sulphur deposit, the twins on (101) are often gathered into radial-fibrous and rosette aggregates. They were seen on large sulphur crystals crusted with pyrite.

The growth of twins. As noted long ago, a twin may be several times larger than untwinned crystals. The cause was first established by F. Becke in 1911. He showed that a twin becomes large because it mostly grows in the direction of the re-entrant angles, where the environment is most favourable. But this angle favours growth only if it coincides with the general direction of the twin edges. The twin then builds up rapidly and elongates towards the re-entrance angle. This explanation clearly refers to the findings of large twins of quartz, calcite, gypsum, dolomite and other minerals.

It should be noted that the earlier studies were mainly concerned with the effect of one re-entrant angle on the twin habit but not with the convergence of several re-entrant angles coinciding with the general direction of edges of both twin individuals. The sulphur twins from the Ciscarpathians are interesting in this respect. They grew together with common sulphur crystals but are quite prominent because of their size.

Both the rate of growth and the size of twins appear to depend directly on the number of re-entrant angles. Thus, their number at the apices of roughly 2-cm twins is larger than in the case of smaller twins. But these angles affect not only the size of twins but also their shape; they selectively favour either the outgrowth or wedging-out of faces. The faces that have received an advantage of prevailing growth gradually wedge out, while the opposite faces of the same simple form become larger and predominating. If the re-entrant angles are located, as though, at the side the twin never builds up along the *c*-axis but along the *a*- and *b*-axis and to become nearly isometric.

Still mysterious are the modes of origin of twinned crystals in general and sulphur twins in particular. That these modes are exceptional follows from the fact that the relative proportion of sulphur twins is low. They were chiefly noted at the Rozdol'skoe deposit. From south to north, the ratio of twins to single sulphur crystals decreases here from 1 : 30 to 1 : 400. The twins on (101) were found most frequently. The external form of such twins is also rather persistent; it was nearly the same at all sulphur deposits, with a slight variation. Also, all twins are found only at sulphur-rich deposits. It appears that only there the supersaturation of the sulphur-precipitating solution had reached a critical value at which sulphur seeds could have touched each other in the twinning position. The moment of contact was determined by the structural similarity of the contacting planes. After a group of sulphur particles had casually taken, not their proper but symmetrical twinning position, the re-entrant angles between the contacting planes played a decisive role. These angles became places of preferable precipitation of the new sulphur particles. So the twinning made the crystal grow easier.

Sulphur deformation. Let us discuss another wonderful property of sulphur—its capability to deform under outside stress. We met with this interesting phenomenon 30 years ago, at the very start of native sulphur studies. Our early knowledge of the sulphur from the Rozdol'skoe deposit began with a finding of specific, bent sulphur rods of small size, which resembled hooks. We even didn't identify them with sulphur. Later, the deformed features were established among sulphur crystals of any habit type, their parallel intergrowths and twins.

Lamellar sulphur individuals are deformed most easily among crystals. They are located between two calcareous walls and look like curved paper sheets. Crystals with bent dipyramidal and prismatic faces are scarce. The deformed sulphur individuals are always attached by their ends to the opposite sides of the vugs they line or to the crystals of other minerals. Parallel sulphur crystal intergrowths with deformed individuals are also located between two buttresses.

Among twins, those on (101) are deformed most frequently. As mentioned above, they grow rapidly in the direction of the wedging-out re-entrant angles ahead of other crystals. Some reach the opposite wall of the vug, with minerals on it, and abut against and become adhered to these minerals with their apices.

An interesting feature of the curved sulphur polyhedra is that their faces are nearly always covered with striations—a system of parallel or intersecting straightline grooves. Prism faces are striated in the curved dipyramidal crystals; some of the faces are covered with oblique striations, others with straight, longitudinal. In parallel intergrowths, the striations are most frequently found on dipyramidal faces. Interestingly striated are the faces of the dipyramid {111}. Some faces are not planes but consist, as it were, of segments tilted insignificantly, roughly by hundredths to tenths of a micrometre, relative to each other; so they look like a mosaic. The striations more often cover the whole face, their direction coinciding in different segments of the mosaic.

Less common are the faces composed of several segments with non-coinciding striations. And even less common are the faces some segments of which are covered with non-coinciding striations while others are quite smooth, mirror-like. The most curved part of the face may be free of striations, while the rest of it may be covered with intersecting ones. The same striations are characteristic of the faces of a dipyramid {111}, which makes the twins on (101) look rod-like. Where some twins are bent to a maximum, the striations widen and get the appearance of narrow faces the reflection from which takes place simultaneously with

Deformed lamellar sulphur crystal

that from the apex-located dipyramidal face of the second individual. The striations on the neighbouring faces of the twin are interrelated; they change orientation on passing from one face to the other, as if outlining a certain plain or its part. A characteristic feature of these striations is that they cover twin faces unevenly: some are striated wholly, others partially. The striations may not reach the edges between the faces but die out somewhere in the middle of the face. There occur not only continuous striations but also discontinuous ones, resembling dash lines.

According to Vernadsky [1902], striations are manifestations of an important property related to surface energy. In his opinion, the striations are oriented in conformity to the least surface energy in this plane. A characteristic feature of a sulphur polyhedron the faces of which are striated is that its growth was constricted. Hence it is deformed to a variable extent, whereas the faces of crystals and twins that grew freely are not striated.

What is the nature of striations? Since they develop only in plastically deformed individuals, they are due to gliding of crystalline matter. Part of the crystal is displaced relative to another part on planes parallel to certain nets of the crystal lattice. The displacement is marked on crystal faces by the relevant striations.

The gliding deformation in one direction on the plane of a dipyramid $\{111\}$ was first noted for sulphur crystals by the German scientist Mügge. The author's experience confirms this phenomenon. In parallel intergrowths, the striations that bound the plane, or its part, are parallel to the face (111) in one direction. The same plane and direction are present in the curved twins. But it is somewhat difficult to determine the elements of gliding in them, because each twin has two individuals. The intersecting striations on the faces point out that the crystal parts move in several directions.

It should be noted that gliding is often far from being uniform. It is not infrequently accompanied by bending of gliding planes or by their rotation. In both cases, the lattice changes its initial position. So we tried to find out to what extent the gliding in sulphur polyhedra is uniform. With this aim, X-ray diffraction patterns were obtained for striated and smooth sulphur crystals. The results show that the lattice of the former is variously deformed and that of the latter, is not. The plastic deformation of sulphur resembles in this respect an interesting kind of plastic deformation described by the physicists Stepanov and Donskoi. The essence of this phenomenon, called lamelling, is that when a rock salt rod is deformed, it first experiences gliding and then breaks into several nearly parallel lamellae. The X-ray diffraction pattern of a deformed sample shows blurred patches, and according to the above authors, these suggest that one part of the crystal turned relative to the other.

As to sulphur, we have come to the conclusion that its crystals underwent processes similar to lamelling, which was preceded by gliding on the plane of a dipyramid {111}. Indeed, as in lamelling, the sulphur sample breaks into several parallel parts bounded by gliding planes. Since the deformed sulphur objects are insignificant in size and the broken-out lamellae delineated by gliding planes are even smaller, the angles of their relative rotation cannot be determined even under the microscope. But the diffraction patterns of deformed samples confirm that such rotation, that is the disturbances in the sulphur lattice, does take place.

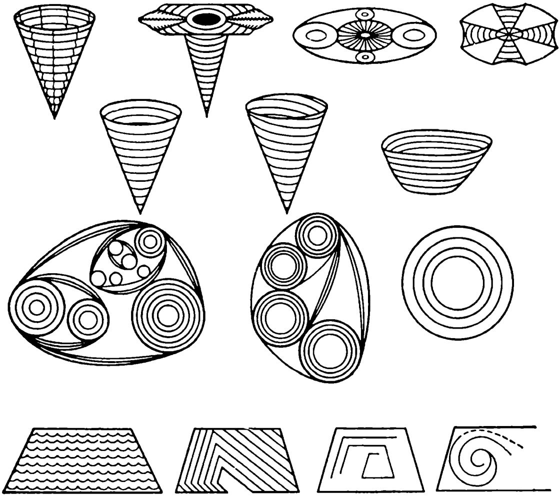
The gliding striations on the sulphur in druses first appear at the close of growth just when the growing sulphur polyhedra touch the druse walls. The vigorous gliding of sulphur crystalline matter is the result of subsequent cavity contraction and deformation. Rock pressure—a complex process with many variables—plays a certain role in this. The character (density and depth) of the striations appears to depend on the stress acting upon the sulphur polyhedron. The deforming force is also a function of the size of the individuals constituting the sulphur intergrowth and the number of their points of touch with the druse walls. This explanation does not account, however, for discontinuous striations (resemble thin dashed lines) on some faces of the deformed individuals.

Dislocations. Crystals owe their existence to their own defects, that is to any structural disturbances, such as lapses in the lattice, impurities and dislocations. The presence of defects makes the distinction between so-called crystal and ideal crystal lattice. The English theoretical physicist V. Frank suggested in 1949 that a non-disappearing step with spirally arranged layers is present on the face of a crystal. V. Frank attributed this step to a disturbance of the crystal structure and called it helical dislocation.

The helical dislocation can be regarded as a partial offset in a crystal. A two-sided angle that forms on the growing face does not disappear when new particles are attached but merely moves over the helical surface. So the crystal builds up through a continuous spiral layer. The centre of the helix is a point at which a linear defect in the crystal body intersects the surface. The Academician B. Vainshtein compares the helical dislocation to a many-storied garage with a spiral car passage inside. Each storey is an atomic plane, while the axis of passage with the adjacent parts of the curved planes is a dislocation.

Such helical growth is only slightly characteristic of sulphur crystals. The exits of helical dislocations can be found on the plane (001) of tabular and lamellar crystals. As the crystal is growing, sulphur particles are attached to the step and lengthen its plane. One large clockwise helix or several small helices, 500 to 1 000 Å high, are normally located on the face. The helices are variable in shape. The small ones are more perfect than large. There were noted winding and polygonal helices, indicating that the layers are anisotropic.

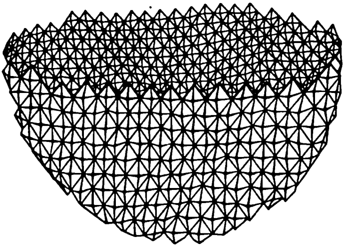
Vicinal forms—geometrical nodes and pits on the faces of sulphur crystals—are also of a dislocation nature. Large vicinal nodes are produced by summation of a series of elementary nodes in areas of concentration of screw dislocations. Some nodes are derived from a rapid local growth of the face around a defect—an inclusion caught by the crystal.



Growth pits on sulphur crystals

As a rule, the new growth layers originate more rapidly around this inclusion. As to the sulphur crystals, the plane (001) grows mostly by way of vicinal forms. Such forms occur as tetra-, penta- and hexagonal lamellae, which grow out until they touch one another to cover much of the face.

The pits are hollows of growth at places of dislocation that are distinctly seen only on the sulphur crystals from the deposit in Syria. The dislocation growth mechanism is typical of all the principal faces that bound sulphur crystals. The hollows of growth occur both in the form of small hollows and more large pits, intruding deeply into the crystal.



A "sulphur cup"—an intergrowth of sulphur crystals from the Giik-Salgan Cave

The crystal habit, which is always a function of the structure of material, depends on physicochemical factors. A great body of data has been collected to date on the shape of natural crystals, but it is rather difficult to assess on this basis the effect of particular physicochemical factors on the crystal habit. Let us illustrate this. Many faces of sulphur crystals are not surfaces that must be produced by normal crystallization. Some of them are so far from being perfect that they should not possibly be called faces. The bounding surfaces of sulphur crystals are then formed by numerous small dipyramidal crystals the edges of which are as long as 2 mm. These crystals are oriented identically with the sulphur crystal the outer zone of which they constitute. Their faces are smooth, that is have no dislocations. The crystals are so arranged that each is overlapped, so to say, by a neighbouring crystal. This, in essence, is an aggregate of sulphur crystals that have grown together in such a way that the aggregate resembles one big crystal. Why they grow in this way is still unknown.

Microbiological Sulphur Accumulation

Microorganisms play a large role in the migration of many chemical elements. They can make the chemical and mineral transformation that cannot be carried out by higher plants and animals, and this further underlines their leading role in the cycle of matter on the Earth.

The microorganisms that produce elementary sulphur are called sulphur bacteria.

The autotrophic organisms of this kind, that is those consuming inorganic compounds to synthesize from them carbohydrates with the help of solar or chemical energy, are widespread in soil and in fresh and sea water. Some species of bacteria are found in hot mineral springs (temperature over 80 °C), and some survive in a 10% sulphuric acid environment. Sulphur bacteria are divided in two groups by the mode of sulphur deposition.

The first group comprises thionic bacteria—the aerobes *Thiobacillus thiooxidans* and *T. thioparus*, and also the purple anaerobe Chromatium. They oxidize the sulphide to elementary sulphur by laying it down outside their cells, in the environment. The microbiologist M. Ivanov shows convincingly that hydrogen sulphide is oxidized to sulphur with the participation of *T. thioparus*, which lives at pH = 3-9.5. The oxidation mechanism is rather complex in this case.

The sulphide sulphur is oxidized as follows:

$$S^{2-} \rightarrow S \rightarrow S_2O_3^{2-} \rightarrow S_4O_6^{2-} \rightarrow SO_4^{2-}$$

Only the oxidation of sulphide sulphur has been proved experimentally. Just like sulphur bacteria, purple *Chromatia* produce extracellular elementary sulphur. The energy generated by sulphur oxidation (about 49 kcal) is used by microorganisms to assimilate carbon dioxide.

N. Yushkin was first to describe the biological origin of sulphur. It is first liberated as minute particles into the water. These then adhere to one another to produce larger accumulations which later give rise to small perfect crystals. The crystals either remain suspended in the solution or become attached to the walls of cavities where they grow further.

The second group of bacteria consists of colourless (*Beggiatoa*, *Thiothrix*) and coloured (*Chlorobium*) autotrophs, which settle down sulphur inside their cells. The first two microorganisms need for their life aerobic conditions and carbon dioxide. Some bacteria of this group can oxidize during a day four times as much hydrogen sulphide as their weight. The energy for the life of *Chlorobium thiosulphatophilum* is provided by the reaction

$$2H_2S + CO_2 \rightarrow (CH_2O) + H_2O + 2S$$

With little sulphide sulphur in the environment, the energy required by the cells is obtained from oxidation of the elementary sulphur in the granules to its sulphate.

The author found sulphur segregations that look like confervoid sulphur bacteria in the sulphur-bearing limestone from the Ciscarpathians. Under the microscope, these were sticks or files of different lengths, often coupled, aligned or intricately bent.

The formation and deposition of sulphur was closely studied in some lakes of Kirenaika. The water flowing into these lakes contains enough sulphate to support *Desulphovibrio desulphuricans*, which participates directly in the production of much hydrogen sulphide. Large colonies of photosynthesizing bacteria, among them those of *Chlorobia*, have been found at lake margins. They further oxidize the hydrogen sulphide produced by *Desulphovibrio desulphuricans*. The sulphur derived from *Chlorobia* is deposited on the lake floor to form a thick bed. The reserves of such sulphur only in one of the lakes are estimated to be 2500 t—approximately 100 t of sulphur a year.

A completely new approach to assessing the role of living matter in the geological history of the Earth's crust and in the geological processes in it is now ripening. This was emphasized at the 8th International Congress on Organic Geochemistry held in Moscow in 1977.

Contaminating Elements in Sulphur

Although sulphur crystals seem clear, all of them contain little impurities. These are tiny mineral grains caught by the crystallizing sulphur. The contaminating minerals were found in insoluble residua. Scarce in sulphur are selenium, tellurium and arsenic. The form in which some chemical elements are present in sulphur has not been established as yet. The native sulphur in sedimentary rocks more often contains much calcium, silicon, magnesium, sodium, iron and aluminium. The same elements are also most characteristic of volcanogenic sulphur, but the amount and order of their abundance are somewhat at variance: silicon, aluminium, magnesium, calcium, iron and sodium.

The sedimentary sulphur contains more calcium than any other element (up to 5%). This is a mechanical calcite impurity caught by crystallizing sulphur. Cryptocrystalline sulphur is generally rich in silicon and aluminium. Their carriers may be volcanic glass, plagioclase, biotite, quartz, glauconite and amphiboles, as evidenced by the insoluble residua left after sulphur dissolution. The perceptible amounts of magnesium in the sulphur are due to some dolomite and clay minerals present in it. Sodium is rather often found in the sulphur from deposits enclosed in sulphate-carbonate rocks. It may well be part of fluid inclusions in sulphur crystals. The iron content of sulphur does not generally exceed 0.1%, being only occasionally equal to 1%. The enhanced iron content of sulphur is due to a glauconite impurity.

The sulphur from sedimentary rocks contains more impurities than that from volcanic rocks. The latter lacks lithium, beryllium, potassium, rubidium, caesium, gallium, tin, molybdenum, nickel, cobalt and antimony. The concentration of these elements in sulphur is variable or insignificant, and the ways of their migration into the sulphur are unknown. It cannot be ruled out that the sulphur catches microelements from subsurface water.

Titanium, vanadium, manganese, copper, silver, strontium, boron, zinc, zirconium, lead, chromium, arsenic and selenium have been noted in the sulphur from both groups of deposits, though in different amounts. The content of chemical elements in the sedimentary sulphur depends on their amounts in groundwater, while those in the volcanogenic sulphur, on their amounts in volcanic gases. No further elaboration has been made in this field.

Out of toxic elements, selenium is worth attention; it occasionally concentrates in native sulphur in amounts exceeding its crustal average. The high concentration of selenium can make an animal or a man seriously ill. We shall describe an event happened in the vicinities of a mine in the Ghost Valley, northwestern United States.

All of the plants that grew in the valley were poisonous, and therefore the indians believed that the valley was bewitched by vicious ghosts. The white settlers disbelieved them. They had ploughed land in Ghost Valley and grew good crops of wheat, corn and oat. But the colonists were joyful not for long. Soon an unknown disease began to spread among them and their domestic animals. It caused blindness, hair loss and death from exhaustion. The medical aid was useless. The cause of the mysterious disease was revealed only in the early 1920s. It was found that the soil in Ghost Valley contained an increased amount of selenium. Plants digested it "by mistake". The point is that the amino acids of plant proteins contain sulphur. But the plants do not discriminate the elements of one and the same group of the Mendeleyev Periodic Table in their food. They confuse selenium with sulphur, calcium with strontium, and magnesium with barium. The replacement of sulphur by selenium does not affect plants, but causes serious damage to the metabolism of man and animals.

Some plants contain much more selenium than soil does. The concentration of selenium in ashes after burning of the plant that grew on a soil with 0.001% Se may reach a value of 5%. This is a rather high value if we take into account that 1 kg of selenium costs about 100 dollars.

Sulphur Isotopy

The isotopic compositions of sulphur, carbon, nitrogen, lead and other chemical elements are now used to solve some geological problems. Because they have different atomic weights owing to the different number of neutrons in their nucleus, the isotopes of one and the same element behave differently in one and the same process; in particular they exhibit unequal diffusion rates, and adsorption and chemical activity. These insignificant distinctions lead, in certain physicochemical processes, to isotope partition, the value of which is reliably measured with a mass spectrometer. The degree of isotope partition of the chemical elements depends on specific natural conditions. Hence, if we know the principal processes leading to the partition of the isotopes of some element and the isotopic ratio for this element in a sample, we can judge upon the physicochemical conditions of formation of various minerals.

Sulphur has four stable isotopes with the following approximate relative abundances in terrestrial materials; 95% ^{32}S, 0.77% ^{33}S, 4.2% ^{34}S and 0.0017% ^{36}S. It is most convenient to determine the ratio of two most common isotopes, $^{34}S/^{32}S$, or, as said frequently, the heavy-to-light isotope ratio. Two other ratios, $^{33}S/^{32}S$ and $^{36}S/^{32}S$ are of interest only in relation to extraterrestrial objects.

Since the sulphate rocks undergo biogeochemical alteration with the formation of native sulphur, a truly geochemical phenomenon occurs in nature—partition of stable sulphur isotopes. The basic process responsible for the variation in the sulphur isotope composition of sulphur ores was bacterial sulphate reduction to hydrogen sulphide. In its turn, the isotope composition of hydrogen sulphide depends on the percentage of the reduced sulphate and the rate of sulphate reduction. As the relative proportion of the sulphate consumed is rising, both the residual sulphate and the hydrogen sulphide derived from it become isotopically heavier.

The data now available indicate that the sulphur isotope composition tends to become heavier as sulphur ore formation is in progress. Powdery (dispersed) sulphur is most light weighted and so earliest. The value $\delta^{34}S$, which is a difference between the contents of ^{34}S in the sample and the standard, varies between +14.3 and —16.7‰. Hence we can postulate that the powdery sulphur is one of the first products of bacterial sulphate reduction, since the lightest hydrogen sulphide originates early in the sulphate reduction.

The next sulphur generation, cryptocrystalline, is markedly enriched in ^{34}S as compared with the powdery variety. The $\delta^{34}S$ is in the range from +16.4 to —3.1‰. The same is true of the sulphur from the pseudomorphs of it (and calcite) after sulphates. In two sulphur-calcite pseudomorphs, $\delta^{34}S$ is equal to +8.3 and +9.3‰, the $\delta^{34}S$ for the initial anhydrites being +8.3 and +11.1‰, respectively. Both analyses refer to the sulphate being replaced by a sulphur-calcite aggregate with a complete (or nearly complete) transition of the sulphate into native sulphur.

A substantially different, heavier isotope composition than that of the grey powdery and cryptocrystalline sulphur is characteristic of fine- and coarse-grained sulphur varieties. The $\delta^{34}S$ for this sulphur varies between —0.1 and +22.2‰. The causes of the sulphur becoming heavier are still unknown.

It follows from the above that the variation in the isotope composition of native sulphur is a criterion to derive the order of its formation in sulphur deposits.

Sulphur As a Mercury Mineral Settler

Sulphur and Mercury. People became familiar with these elements many centuries ago. In Ancient Egypt, metallic mercury and its basic mineral, cinnabar was used as early as the third millenium B.C. Pliny the Elder mentions them in his "Natural History", which means that ancient Romans knew about these elements. The mysterious properties of mercury stroke the scientists of India, Egypt, and China, and the alchemists of the Middle Ages. Arabian chemistry referred to mercury as "mother" of metals, and to sulphur as "father". The great Central Asian scientist Ibn Sina (980-1037) also believed that all metals were derived from mercury and sulphur. Alchemists tried to find the way to convert simple metals to gold and silver, and to cure all diseases with the help of mercury purportedly contained in a fantastic "philosophical stone". Scarlet cinnabar—mercury sulphide—is just the sought-for "philosophical stone". In this way just argued the Franciscan monk Brother Roger, known in science as Roger Bacon (about 1214-1292). Ancient Arabs called cinnabar "dragon's blood".

Much is puzzling in mercury properties and behaviour. Metallic mercury is mineralogically unique; it is produced by certain geological processes and occurs in a specific environment, nothing like that in I.A. Efremov's science-fiction story "Lake of Mountain Ghosts". Cinnabar and very rare metacinnabarite are the almost only mercury sources. Both minerals are identical in chemical composition (86.2% Hg and 13.8% S) but differ in properties.

We have managed to see interesting relationships between both mercury minerals and sulphur in some sulphur occurrences and deposits (Dnieper-Donets depression and Gaurdakskoe deposit).

Mercury occurrences have been noted in the Adamovskii, Korul'skii and Berekskii salt domes. Mercury mineralization with up to 1% Hg was found in boreholes on the domes of the Slavyanskaya group of deposits in 1961.

The mercury occurrence of the Adamovskii salt dome is restricted to caprock breccia and Lower Permian sandy rocks. It is in the zone of regional faults that are ore channels and controls. The occurrence is cut by fissures, which may have served as conduits for gas emanations escaping from the depths of the Earth.

The cinnabar with the accompanying calcite, sulphur gypsum and hard bitumen concentrates in nestles, metasomatic dissemination zones, zones of stockworks and veins, leaching cavities and contraction cracks.

The cinnabar is coloured deep red, crimson and scarlet red. It occurs as aggregates of small grains closely contacting each other and since that difficult to identify under the microscope. The cinnabar is closely associated with calcite and sulphur. It generally forms a thin crust enveloping calcite grains and fills interstices between the grains and cleavage joints. There is a feeling that cinnabar replaces calcite. Such relationship was described by H. Koroleva in 1953.

Spherical cinnabar, up to 0.5 mm in diameter, is of more limited distribution. It does not differ in outer appearance from spherical sulphur, which covers calcite as fines. Fine-grained sulphur aggregates can always be found in some or other amounts in the spherical cinnabar. It follows then that native sulphur participated directly in the formation of these cinnabar occurrences. The chemical composition of cinnabar from the Adamovskii dome is as follows: 80.24% Hg, 15.04% S, and 3.35% Fe.

The mercury mineralization related to young karstic cavities in the gypsiferous units of the Gaurdakskoe sulphur deposit is of primary genetic significance for the mercury deposits of the Soviet Central Asia ore province.

The mercury mineralization in the Gaurdakskoe deposit was found in a karst cave reached by mining openings. Like the whole deposit, the cave is located at the southwestern pericline of the Gaurdakskoe anticlinal uplift near the deep-seated Uzunkudukskii fault. The cave is in the uppermost part of thick (up to 400 m) bituminous limestone of the Kugitangskaya Formation (Oxfordion) and in the limestone and gypsum-anhydrite markers of the Gaurdakskaya Formation (Kimmeridgian). Some of the cavities are at the contact between these formations, extending at places into sulphur-calcareous rocks (sulphur ores); others extend along faults, and fracture and breccia zones that control the sulphur bodies.

The walls of cavities are encrusted with sinter forms of gypsum: stalactites, drapery, septas and anthodites (stony flowers), and at places with rock milk sinter. Grey jelly-like masses containing 90% native sulphur (sulphur milk) occur in some hollows in the cave floor. Fine sulphur disseminations are also found on the walls. The sulphur mineralization is becoming poorer up the walls of the cave.

The principal mercury mineral is metacinnabarite, which coats not only the gypsum but also the clay accumulations. This is a greyish-black mineral with a metallic lustre. According to a spectral analysis, it contains (in addition to mercury) 0.01% Al plus Fe, 0.03% Si, 0.001% Mg plus Mo and 0.003% Na. Its Debye crystallogram is similar to the reference one (strong reflections 3.396 (10), 2.068 (10) and 1.762Å (10)).

Cinnabar is less common. There are two cinnabar varieties. The first, older, concentrates in large (up to 15 cm) secondary gypsum crystals grown as horns over the upper side walls of galleries. Because of this, the crystals have become untypically red coloured.

The cinnabar occurs as thin (hundredths to tenths of a millimetre) films consisting of mutually adjoining grains of the same size. The films coat the walls of cavities, which are numerous in the gypsum. Some cavities are mantled by the same films of yellow sulphur and secondary (after cinnabar, further unidentified) minerals coloured canary yellow. The latter are due to cinnabar oxidation by sulphate rocks.

The second-generation cinnabar is derived from metacinnabarite alteration. Its colour varies between dark red and grey-brown red. Like the metacinnabarite, it occurs as fine-grained concentrations. Cinnabar diffraction patterns show the following reflections: 3.36 (10), 3.16 (7), 2.86 (10), 2.08 (8), 1.98 (8), 1.76 (7), 1.73 (8) and 1.68 Å (7). Hydromica and hematite, nearly invariably associated with the cinnabar in its commercial concentrations, are appreciable in the areas of mercury mineralization.

The mode of origin of cinnabar and metacinnabarite is as follows. Mercury is a subcrustal product that forms as a mineral of its own in the uppermost crust, accessible for studies. The restriction of mercury occurrences to tectonic structures indicates that the enhanced mercury content is due to the reactivation of the deep-seated faults that served as conduits for mercury-bearing gas emanations.

The enrichment of gas in mercury is observed on the active volcanoes on the Kurils and in Kamchatka. Some consider this form of transport to be basic. N. Ozerova et al., are fair in noting that the absence of hydrogen sulphide favours the high mercury content of the gas phase. It is hydrogen sulphide and native sulphur that settle down mercury minerals. Interaction between the gas emanations saturated with respect to mercury and hydrogen sulphide common in sulphur deposits favoured metacinnabarite deposition. The mercury vapour interacted directly with sulphur to produce cinnabar where hydrogen sulphide was absent for some reason but the native sulphur derived from its oxidation was in great amounts.

The geologist E. Yanchinskii, who discovered mercury mineralization in the Gaurdakskaya Cave, notes that the formation of cinnabar and metacinnabarite can be observed even now. According to him, the lower storey of the cave was flooded from October 1977 to July 1978. In July, after the water level fell, the metacinnabarite was markedly more in amount in many places of the Onyx Pass and on the walls and stalactites of the Fairy Tale Hall. Cinnabar powdery coating appeared beside the metacinnabarite on the walls of a large passage near the Crossroad Hall. Only metacinnabarite has earlier been found here and that in much lesser amount.

Why is the mercury mineralization restricted in the Gaurdakskoe sulphur deposit to a small cave and not to the whole of it but only to its separate localities? Is it possible for the cave to be related to a fault deeper than other ones in the rest of the deposit, for the volatiles of other metals to rise along this fault together with mercury vapours? The questions remain to be answered, and many other surprizing facts have been revealed in studying the Gaurdakskaya Cave.

Sulphur Caves

Sulphur caves are unique in many respects. Let us describe three of them: the Maiden Cave on the shore of the Volga River, the Sheki-Ekhkkhekh Cave in Checheno-Ingushetiya and the Giik-Salgan Cave in Dagestan.

Like other caves of the Syukeevskaya Group, the Maiden Cave is in Permian dolomite 25 km downstream from the Kama junction, higher than the low level of the Volga River. The dropping water inflow from the dolomite contains upto 51 mg/l hydrogen sulphide. With a free oxygen access, the hydrogen sulphide decomposes to powdery native sulphur laid down as small stalactites and stalagmites.

Sheki-Ekhkkhekh stands for Chechenian "sulphur cave". It is in the right-hand side of the Sharo-Argun River gourge, 6 km from the Ulus-Kert village, in Jurassic and Cretaceous carbonate rocks, immediately below sulphur springs, 15 m above the river bed. The cave is 3 m long, 4 m wide and about 3 m high. Its walls and ceiling have prominences and niches. The floor is littered with small limestone fragments. Druses of transparent gypsum crystals and powdery coating of dark-yellow native sulphur are clearly seen on the ceiling and walls. Wet gypsum areas are observed on the walls and especially on the ceiling of the cave.

The Giik-Salgan Cave is in the gourge of the same name (approximately 300 m above its bottom), 30 km south of the city of Makhachkala. It is 15 m in length, 4 m in width and about 3 m in height. It may be a former opening to mine rich sulphur ores. Its walls and ceiling are uneven, with prominences and niches encrusted with light-yellow sulphur crystal intergrowths. Thin sulphur crusts often grow directly on the fine-grained gypsum derived from sulphuric acid action. One feels a strong odour of hydrogen sulphide; it is dangerous to stay here. Sulphur mineralization has been noted in precipitous rocks above the cave and near its mouth.

Ubiquitous and Diverse

No one mineral family has been useful for men as long as silica minerals. They are part of nearly all rock types and are found at literally every step. These minerals are common quartz and its following varieties: rock crystal, amethyst, smoky quartz (rauchtopaz), citrine, pink quartz, avanturine, prase, and hawk's, tiger's and cat's eyes. The microcrystalline silica varieties are chalcedony, quartzine, carneol (carnelian stone), sard, chrysoprase, blood-stone and agate, and amorphous are precious, fire and worthless opal. Silica also occurs as pseudomorphs after wood. What a wonderful silica! It can take quite an unexpected appearance.

Quartz—trigonal silicon oxide stable at low temperatures—is one of the most common in the Earth's crust and of the best studied minerals. From a manual chopper of the so-called "Stone Age Culture", the first tool of man, to a piezoelectric quartz plate, without which modern radio engineering cannot exist—that's the glorious field of quartz application. No other mineral compound has ever attracted such keen scientific interest. No any other mineral has ever played such an outstanding role in the making of mineralogy, crystallography and physics as quartz. Its importance in man's life is hard to overestimate.

First artifacts in the world were made out of small quartz pebbles, which were treated by way of cleaving at acute angle to produce cutting or chopping objects. They were found in the vicinity of Lake Rudolf, East Africa. There were also found there the remains of a "living" surface in a tuff layer whose K-Ar age is 2.6 m.y. This relatively limited area of the Kenyan rift zone should be regarded as a kind of an ecological niche in which the first man's ancestors appeared, being able to manufacture primitive stony artifacts. *Homo erectus* (man with a straightened back) could roughly treat stones, use fire and protect himself from bad weather as early as 1.5 m.y. ago. He later spread gradually from Africa into Europe and South Asia.

Quartz is nearly wholly silicon dioxide (SiO_2). Variation in its chemical composition is very narrow. Low-temperature trigonal quartz is converted to a hexagonal modification at 573 °C. This one is transformed at 870 °C into α-tridymite, which then passes at 1470 °C into α-crystobalite with the melting point of 1710 °C. Its hardness is 7 on a scale of 10 (few harder minerals are in nature). The density is 2.65-2.66 g/cm^3. Quartz is well transparent for infrared and ultraviolet rays, is heat resistant and is a poor electrical conductor. It is chemically stable, dissolves only in spar acid; as on glass, various patterns and even pictures can be drawn on it. It is strong; a weight of several tonnes is needed to crush a quartz cube of 1 cm^3.

The piezo effect of quartz—an electrical phenomena observed during the extension and compression of its crystals—was discovered in 1880. The result was broad quartz application to modern radio engineering. It was used to produce frequency stabilizers, filters and resonators, and plates to receive and transmit ultrasonic oscillations. Most quartz crystals are twinned, mosaically disposed, contain fluid and solid inclusions, have distinct growth zones, and so on.

Rock crystal, bluish quartz, chalcedony, quartzine and precious opal occur in sulphur deposits.

Rock crystal is quartz transparent as air, colourless as tear and cold as ice. That quartz is like ice was noticed long ago. Man of antiquity took it as ice that can thaw no more. Pliny the Elder (1st century A.D.) postulates in his multiple-volume "Natural History" that rock crystal forms under the action of strong cold.

Owing to its high hardness, purity and brightness, rock crystal has been since long ago not only a cult object but was also used to manufacture ornaments and stone cutters. It was taken as a stone of perfection as early as the 3rd century B.C. In myths and legends, the gods on Olympus drank ambrosia only from crystal cups. Vases, cups and other vessels, many artistically incrusted with silver and gold, were cut from large rock crystals at the times of antiquity and the Middle Ages.

The art of rock crystal cutting was at its peak during the Renaissance. It was used to make not only traditional vessels but also rings, boxes, various signets, statuettes and desk sets. A unique cut-glass samovar of Peter the First is in the Armoury, Moscow Kremlin. It can be scorched hot and submerged in cold water and nothing will happen to it.

As mentioned, in examining rock crystal polyhedra, the Dutch scientist N. Steno was first to reveal the secret of crystal growth. It is still a mystery how the famous Skull of Death was cut out of a quartz crystal, in defiance of all laws of crystallography and crystallooptics, long ago in ancient times. It was found in 1927 by the American archaeologist Ph. Mitchell-Hodgess in the course of excavation of a town in Honduras jungle. The skull is mirror-finished. Lenses and hollow ducts cut inside the skull produce striking light effects. Maya priests hypnotized the believers with the help of this Skull of Death.

The rock crystals in sulphur deposits chiefly concentrate high in the productive unit. Non-sulphurated limestone is especially rich in them. Quartz occurs here as irregular granular concentrations, isolated crystals or their intergrowths in the form of small (up to 1 cm in diameter) "rosettes". The crystals in the "rosettes" radiate from the growth centre; they occur as short (up to 0.4 cm) hexagonal prisms.

Small (up to 15 mm) isometric rock crystals, which are as transparent as fresh water and as brilliant as faceted gemstones, are more seldomly encountered. Such polyhedra form where one, $\{01\bar{1}1\}$, but more frequently the other $\{10\bar{1}1\}$, or both rhombohedra prevail greatly, the faces of a prism $\{10\bar{1}0\}$ being absent nearly completely. Where the faces of both rhombohedra are developed equally, or nearly so, the crystals look like hexagonal pyramids, having a distant likeness to diamond. That the rock crystals were in the past widely used in jewelry follows from references to the Cape May and Arkansas diamonds, USA; Bristol and Cornish diamonds, Great Britain; and briancon diamonds, France. Marmora diamonds—1.5 mm crystals with very bright faces—are known from the Eastern Carpathians. They are used without faceting.

In the lower productive unit, rock crystals up to 1.5 mm in size have been found to grow randomly on the surface of large celestite crystals. As many as 15 rock crystal individuals can occur on one celestite polyhedron.

Bluish Quartz

Bluish quartz is known from the Ciscarpathians. Together with light-yellow rhombohedral calcite, it lines small cavities in the non-sulphurated limestone from the Rozdol'skoe deposit. Its crystals look like short rods (up to 0.5 cm along the threefold axis) and are hexagonal because the rhombohedras $\{10\bar{1}1\}$ and $\{01\bar{1}1\}$ are developed almost equally. The quartz is younger than the calcite. It generally overgrows on calcite aggregates and separate crystals, the threefold axes of both minerals being more often mutually parallel. The prismatic faces are covered with horizontal (oscillation-type) striations.

The quartz is pale coloured, varying from milky to smoky blue. The nature of the blue colouration is still debatable. Some believe that it is due to a very fine TiO_2 impurity. Indeed, the milky-blue quartz contains up to 0.001% Ti, while no titanium has been found in the water-transparent crystals of this mineral.

Chalcedony

Quartz occurs not only as beautiful crystals but also as massive cryptocrystalline bodies whose thin sections show a fibrous structure under the microscope. The quartz mass is clearly seen to consist of minute fibres normal to the growth surface. They are normally thousandths of a millimetre in diameter and 0.2 to 0.5 mm in length. The fibrous quartz varieties are called chalcedony and quartzine. They are compact, reniform, with a waxy or dull lustre. Another variety is hornfels—opaque chalcedony with casually oriented fibres gathered into fan-like, angular and irregularly shaped aggregates.

Chalcedony embraces quite a gamut of coloured stones each of which has its own name depending on its colouration, pattern and structure. There are more than a hundred of such stones. The chalcedony proper is coloured bluish, yellowish and grey; carnelian, pink or brown-red; sard, reddish brown; chrysoprase, green or apple-green, and so on. Quartzine is more modest in colouration, being mostly pale blue.

Semitransparent chalcedony with a distinct banded structure clearly visible with a naked eye is called agate. In old China, a special amulet was laid on the tongue of a dead during the burial ceremony. It was cut from brown agate in the form of a cicad which was taken for a symbol of resurrection. Those in the early Middle Ages believed that if one carried an amulet or ornament made out of this stone, he became pleasant in society and his speech, more thoughtful and expressive.

Hornfels is dark because it contains appreciable amounts of impurities. Man has been using it since deep in the past; he manufactured from it knives, axes, scrubbers, heads of spears and arrows, and so on. Hornfels was widely utilized to obtain fire through a stroke with a steel bar before matches and detonators were invented. Beautiful temples were constructed, drawings on rocks were made and basalt figures on Easter Island were cut with the help of hornfels.

Chalcedony is easy to cut. Bead necklaces, and stones for ring and pendants have been made out of it for several thousand years. It was used as an ornament of not only cloth but also saddles, harnesses and various arms. Moreover, it was taken as miraculous, for instance as a help in running cases in court and in curing mental diseases and melancholy.

Stone cutting was flourishing as early as the 6th century B.C. The technique of expressing an artistic idea in a small piece of stone was most perfect in intalgios—gems with an incut image—and in cameas, with a cut-out image. No one can rival with them even today in the skill of making, and chalcedony was an indispansable material for cutting gems.

Chalcedony was later treated to make pins, belt-buckles, toilet boxes, caskets, vases, cups and many other things. Nowadays, too, it is utilized widely in stone cutting, in particular to manufacture cabochons (convex stone faceted on all sides) and plates for cheap jewelry, such as rings, pendants and necklaces. Chalcedony is quite lovely in all ornaments.

Perceptible amounts of chalcedony in sulphur deposits occur as concretions and thin (fractions of a millimetre to first few centimetres) layers of flint. Flint concretions are as large as 10 cm along their largest dimension. They are rather variable in shape. Obeying some unknown whims of Nature, the flint occasionally resembles animals (a dove, cat or monkey) or even a strange human face. Its dark colouration is due to unevenly dispersed bituminous matter with a clay impurity. This is so-called patchy flint. It clearly replaces limestone in the sulphur deposits of Soviet Central Asia. The same is also seen in thin sections.

Chalcedony concretions are diverse. Especially interesting among them are ellipsoidal ones reaching in elongation a value of 0.5 m. They are occasionally restricted to a separate bed extending for 4 km. These, seemed to be common, stones are wonderfully beautiful. They are zoned and mostly coloured bluish grey, lylic, grey-brown and milky. Once you cut a concretion skilfully, a picture saved for thousands of years will come to life and sparkle with fantastic colours. Surprising and rich is the internal world of concretions!

The concretions with banded, concentrically zoned and intricately curvilinear patterns are called patterned. They are made up of chalcedony, which can easily be mirror finished. You can see under the microscope that the chalcedony consists of fine-grained aggregates (grey layers) and radial-fibrous spherulites (light-coloured layers). Flint resembles broad-banded agate in both cross-section and structure. One could barely believe that a common stone can be a pleasure for eye, with its beauty and richness of pattern. No use is made as yet of such patterned flints in the stone-cutting industry, but it is in a wide application by collectioners, who cut it to produce little objects (plates, inserts in jewelry and the like).

As beautiful as the above-described flint are chalcedony concretions from the productive unit of the Gaurdakskoe deposit. They occur in chains in rock strata with the formation of rather persistent flint beds. In open-pit mining of sulphur ores, flints are readily separated from the enclosing carbonate rock and accumulate at the base of the open-pit mine. Two types of concretion have been found here. Those containing cavities lined with grey barite crystals, sky-blue celestite crystals and transparent gypsum lamellae are more common. More seldom are concretions of bluish-grey patterned chalcedony. Their bright-polished sections look like marvellous multicoloured pictures of the great painter—the Nature. These are excellent for a collection.

The chalcedony in sulphur-enclosing limestone from the Ciscarpathians occurs as small (up to 0.2 mm in cross-section) spherical segregations gathered into grape-like aggregates. The spheres are radial-fibrous or concentric; some of them are hollow. They nearly continuously blanket the surface of crystalline-granular sulphur.

Quartzine

Quartzine is identical in composition with, similar in properties to, and differs by its longer fibres from chalcedony. Interestingly, it is the differences that make it more akin not only to native but also to sulphide and sulphate sulphur. This is unlike chalcedony, with its shorter fibres, which tends to be akin to calcite. No geochemical essence has yet been disclosed of such selectivity in the behaviour of the two fibrous quartz varieties.

Quartzine was found in the sulphur ores of the Ciscarpathians and Soviet Central Asia. In the former, it is observed in isolated bluish-grey spherulites, their grape-like aggregates, thin (up to 0.5 mm) streaks, concretions and pseudomorphs after celestite crystals. The fine-grained mass of the mineral often contains small cavities lined with transparent quartz crystals. You can clearly see that the bluish quartzine grades into colourless quartz. The quartzine forms grape-like aggregates and is coloured yellowish brown in larger cavities. Where small sulphur crystals occur in the cavities, quartzine spherulites replace them.

Besides the spherulites, the fine-grained mass of the mineral also contains its coarser-grained aggregates, which occur in short streaks as wide as 0.5 mm. These are composed of fan-like quartzine fibres ranging in thickness from 0.005 to 0.1 mm.

Rather large (up to 20 cm) concretions of quartzine and its pseudomorphs, some of them with quartz, after celestite crystals and their intergrowths have been found at the upper levels of one of the sulphur deposits. The aggregates of the replacing celestite are radial-, parallel- and intermingled-fibrous, foliated and pseudolatticed. They are coloured light grey, greyish cream, often nearly white.

The gypsum of the Gaurdakskaya Formation encloses spherulites and concretions the cavities in which are filled either with anhydrite or gypsum or with an alternation of these minerals and quartzine. The concretions range in size from 2 mm to 10 cm. The quartzine is replaced by sulphur streaks, which cut through not only some spherulites but also through entire concretions. It also makes up thin streaks, which replace the limestone.

In the Ciscarpathians, the quartzine replaces not only sulphur but also hauerite, manganese sulphide. The colour of the mineral varies between dirty grey and bluish white. It is a fine-aggregate mass under the microscope, fibrous at places. Besides the replacement of hauerite, the quartzine forms peculiar substitution pseudomorphs in clay. It fills the cavities left after hauerite dissolution and hence looks like octahedra, this shape being unusual for quartzine. The origin of such crystals in one of the mineral deposits of the Ciscarpathians have long remained inexplicable.

Precious Opal

Opal—water-bearing silicon oxide of amorphous or cryptocrystalline structure—has long been known to man. Precious opal was especially popular. Pliny the Elder describes a nut-sized opal of extraordinary beauty, which belonged to the Roman senator Nonius.

We recall that stones have been surrounded by an atmosphere of secrecy, prejudices and horror, since very long ago. According to the views common during the Middle Ages, they, like the stars, were closely related to human life: they guarded those who carried them from diseases and misfortune, poverty and betrayal; they gave strength, and brought peace and happiness. Some believed, for instance, that precious opal can help man to become invisible, regarded it as a curing stone, preventing from the eye disease.

In essence, opal is solidified jelly-like matter composed of water-dissolved quartz. Water, whose amount in solid and dry opal is 10%, exerts an appreciable influence on the outer appearance of the stone, above all on its colouration. Opal can be colourless, transparent as glass and black as coal, bright and lustrous as diamond and dull like wax. A characteristic feature of some opals is opalescence—rainbow brightness, a play of colours when you rotate the stone. The opals are divided by this feature into precious (opalescing) and worthless (without opalescence). Fire opal is another variety. Iron, manganese, nickel and graphite are chromophores (colouring components).

The gem qualities of opal are caused by its unusual properties. The miraculous play of colours was attributed not long ago to a light refraction at thin lamellae. The actual cause of this interesting phenomenon was disclosed with the help of a 20 thousand-magnification electron microscope. The opalescing opal was found to consist of tiny spherical particles (globules) of cristobalite—a low-temperature SiO_2 modification—with unfilled interstices, submerged in a regular fashion into gel-like silica. The particles range in size from 150 to 450 μm. Lovely colouration, the play of colours and other light effects are due to the reflection and dispersion of light from the regularly arranged globules and interstices between them. Some of the colours predominating in the opal are a function of the size of its particles. Thus, the opal composed of small globules has purple opalescence, and that made up of large ones, red.

As mentioned above, opal always contains water, which may then be lost in the air. As a result, the opal may become pale and may even crack and break down. Is it this property that explains why, according to one view, opal causes unhappiness? In the opinion of the American mineralogist C. Frondell, this belief became popular after the publication of Walter Scott's "Anne of Geierstein" in 1829, whose personages believed in the strength of this stone. The French empress, Eugénie, wife of Napoleon III, fashion-setter and organizer of court festivities, was said to refuse from wearing opal ornaments. For the opal not to lose its colour play and transparency, specialists recommend that it be buried in the earth for several years. The stone then loses water but gradually.

The black precious opal is taken to be most valuable. It is called, in its own right, a king of gemstones. The stone is dear because it is sparse and show an exclusively beautiful (diamond-inherent) play of reflected light against a velvet-black, dark-purple, dark-blue, dark-green or dark-grey brown background. Especially scarce are opals with a crimson glimmer against a black background. Each sample is peculiar and beautiful in its own. Deep-black opals are extremely scarce.

In white opal, the colours are not so bright against a white background, which makes it much less expressive and cheaper.

Australia is the largest opal supplier to the world market. Found here was the biggest opal, "Queen's Torch", one of the most beautiful opals in the world. The stone weighs 50.6 g; its diameter is 7.6 cm. A beautiful black opal called "Devonshire" was found in the Lightning Ridge deposit. It is oval-shaped, 5 × × 2.5 cm in size, and weighs about 20 g. Opals without cracks are easy to polish. They are usually cobochoned and inserted into rings. The fire opals are faceted and used in broches and pendants. In the US market, intensively coloured precious opals that are from 1 to 10 carats in size cost in American dollars per carat: 100-1500 for black opals, 25-300 for white opals, and 10-200 for fire opals. Artificial opals are produced in some countries, including the USSR.

Precious opal was found in one of the sulphur deposits as a rare secondary mineral derived from a slow decomposition of quartz-bearing rocks. It is coloured white to pink-white, and has a vitreous lustre and conchoidal fracture. Its pieces range in size from fractions of a millimetre to 2 cm. They are irregular in shape, looking like corrugated plates as thick as 3 mm. The thicker the plate, the brighter and more colourful play it shows. It seems that a small spring-time sun is hidden on the bottom of some lamellae, and shines with all the colours of the rainbow. Take another sample. Here glow numerous bright sparks and red glimmers of light. They dazzle and sear with an icy flame, charm you with sudden northern lights in miniature. Going through several pieces of noble opal, one can admire with their play for hours. Tiny lumps of precious opal with reddish opalescence have been found in benthonite clay derived from the volcanic ashes of the Transcarpathians.

Despite a substantial progress in opal studies, its mode of origin is still unknown. Why was precious opal found only in one sulphur deposit, which is located in an area having an arid desert climate. The rate of opal precipitation is estimated at 1 cm in 200 thousand years. To what extent is it true of precious opal? How do other components present in silica-bearing solutions affect its deposition? These and other questions are still to be answered.

The Mystery of Melanophlogite

Recent studies have shown that hydrocarbons are ubiquitous in the Earth's crust; all their forms of occurrence are interrelated and constitute a single hydrocarbon geosphere. The hydrocarbon compounds and mineralizers interact at different levels and under different physicochemical conditions, making up a single fluid system. The hydrocarbons create a reducing environment of mineral-forming systems.

Hydrogen compounds are mainly present in rocks as isolated inclusions in the crystals formed during the growth and further evolution of minerals, and in fractures, caverns and so-called open voids. Man has long paid attention to inclusions in minerals, more particular to their composition. The Central Asian scientist Biruni (Abu-r-Raihan Muhammad al-Birun) (973-ca. 1050) writes in his treatise on mineralogy: "All transparent minerals are derived from a liquid that becomes a stone, as follows from alien inclusions such as air bubbles and water droplets." The teaching of fluid inclusions in minerals is now a vigorously developing branch of science.

It is important that inclusions also contain hydrocarbons. We'll tell you about one extremely scarce mineral with such inclusions. This is melanophlogite—a little known cubic silica modification found only in the sulphur deposits on Sicily. Its nature has been a subject of debate throughout many decades. And it has long been regarded as a quartz pseudomorph after fluorite or cristobalite.

Melanophlogite occurs as cubic crystals, as long as 2 mm along the edge, mutually intergrown, combined into rounded aggregates and crusts on sulphur, calcite and celestite polyhedra. Unaltered melanophlogite is colourless to pale yellow or to dark reddish grey-brown, with a strong lustre. It is invariably zoned, generally altered and replaced by quartz with ultimate formation of quartz pseudomorphs. The mineral consists of 92.4% silica, 5.7% sulphur trioxide, 0.81% hydrogen and 1.2% carbon.

The sulphur, hydrogen and carbon of the mineral occur in the inclusions as H_2S, CO_2, H_2O and hydrocarbons. Little amounts of these compounds were present in mineralizers and were caught by the growing crystal. The organic matter is anisotropic and frequently determines the birefringence and zoning of the crystal. When heated to 150 °C, the point of organic matter decomposition, the birefringence of the mineral disappears (the refraction index of the mineral with pigment is 1.467 and that of the heated one, 1.425). Without water, under a steam pressure of 200 atm and at 500 °C, it is converted to quartz with some hydrogen sulphide and organic matter. Grades into quartz when simply ground in a mortar.

Hydrocarbon-bearing inclusions arise in a non-uniform mineral-forming medium in which the hydrocarbons are dispersed as minute droplets. When crystals grew, these droplets may have touched the growing faces and become "buried" inside the crystal.

Melanophlogite is an enigmatic mineral. Its specifics are that it crystallizes from solutions that contain not only silicon but also appreciable hydrocarbons and hydrogen sulphide. Such complicated solutions are scarce in the Earth's crust. Other processes may occur at this time, still unknown to mineralogists.

Metalloorganic compounds have also been insufficiently studied and remain puzzling. Let us characterize some of them in short. Natural compounds of magnesium with organic matter have been unknown until recently. They were found in the Kalushskoe potassium deposit, Ivanovo-Frankovskaya Region, in 1973. Like metallic magnesium, the material takes fire on heating and burns with a smoking fire. It melts at 125 °C and decomposes at 445 °C into an organic radical and a magnesium group. Cases are known where it took spontaneously fire in mining openings. Contains 18.08% magnesium and 81.92% organic matter.

The metalloorganic compound occurs as grey crusts, first few millimetres thick, that cover the walls of narrow fissures. Its fracture is uneven to subconchoidal. The lustre is dull; that of very pure varieties is glassy. The hardness is 3-4 and density 1.605 g/cm^3. Refraction indices: $n_p = 1.549$ and $n_g = 1.553$. Dissolves with difficulty in acids and organic solvents. Covered in the air with a grey-white powdery coating that protects it from further weathering.

The magnesium-organic compound is derived from interaction of organic compounds input along the fault with the magnesium component of rocks under superficial conditions. This compound points to organic matter migration from deep in the crust. It is easier to find it if it catches fire spontaneously. In the Gaurdakskoe deposit, the metalloorganic compound was found on gypsum as a black sooty coating. Iron is the principal metal associated with the hydrocarbon skeleton. Many years of exploring sulphur deposits suggest their paragenetic relation to hydrocarbon accumulations.

What is the influence of hydrocarbons on mineral formation in the rock, in particular on the precipitation of native sulphur in it? As is known, this problem has not been discussed as yet. In trying to solve it, the author was of the opinion that hydrocarbons directly participate in the reduction of the sulphate ion to hydrogen sulphide, which decomposes, under the effect of oxygen-bearing water, with the formation of sulphur.

The hydrocarbons penetrated into the Kazanian—the lower Vodinskaya and upper Dubrovinskaya formations (Vodinskoe sulphur deposit, Middle Volga)—after sulphur had been formed in carbonate rocks. Fractured carbonate rocks favourable for sulphur deposition were also favourable for hydrocarbon introduction in them. As follows from the mineral composition of sulphur ores from this deposit, appreciable amounts of hydrocarbons were present in the solutions from which both native sulphur and calcite precipitated. Other evidence for it is zoned sulphur crystals and peculiar phantom crystals of calcite in the ores. The zoning consists in the centrally lying darker core or several zones distinctly outlined by bitumen.

A phantom crystal is a "crystal-in-crystal" form. The phantom is brown bituminous calcite and the host is a colourless and transparent dipyramidal-scalenohedral crystal. Besides the bitumen-rich zones, the sulphur crystals contain considerable amounts of hard bitumen caught by the crystallizing sulphur. The calcite crystals with some bitumen show indications of their slowed-down growth. They have imperfect and unevenly developed faces and curved edges. They differ considerably in this from the outside calcites.

At the sulphur deposits of the Ciscarpathians, information about the presence of bitumen in mineralizers is provided by barite. Its tabular crystals are clearly zoned. The bitumen-rich brown bands are parallel to crystal faces. In the rod-like crystal, its base is coloured brown by a bitumen impurity, while the top is colourless.

This evidence indicates that little hydrocarbons do not impair sulphur origin. On the contrary, rather, their first batches participated directly in sulphate ion reduction to hydrogen sulphide whose oxidation just produces sulphur. The part of bitumen that did not participate in the reaction is absorbed by sulphur, calcite and barite crystals with the formation of zoned individuals. While minerals crystallize from mineral-forming solutions, these solutions are becoming poorer in bitumen. The occurrence of crystals consisting of several zones suggest pulsating introduction of hydrocarbons. Their enhanced contents were noted at the Rozdol'skoe deposit.

The high hydrocarbon content negatively affects sulphur formation in rocks. This is, for instance, one of the main causes of sulphur absence from the Kugitangskaya Formation at the Gaurdakskoe sulphur deposit. A similar picture is observed at the Vodinskoe deposit, where a high bitumen content on the western side of the western segment has caused a sharp sulphur deficiency in rocks.

According to mineralogical observations, a marked saturation of mineral-forming solutions with respect to hydrocarbons prevents new sulphur seeds from origin and the growth of the crystals that were still under formation at that time. This is because the high bitumen content enhances the viscosity of mineralizers and hence greatly slows down the release of mineral particles from solution, and also prevents their movement towards the growing crystal. Sulphur is generated most vigorously where hydrocarbons are introduced in pulses in amounts providing the reduction of the sulphate ion by them.

It should be noted that the chain of sulphur deposits in the Ciscarpathians is restricted to areas of gypsum-carbonate rocks cut by fractures; hydrocarbons may have migrated along them from greater depths. It is in this way that peculiar water "windows" arise, which contain relatively much hydrocarbons. An analysis of gases dissolved in the waters flowing through the Rozdol'skoe deposit indicates that these waters contain much more gaseous hydrocarbons, in particular methane (0.4 vol. %), than the springs outside the deposit ($2.34 \times \times 10^{-4}$ vol. %). Note that the condition needed for appreciable native sulphur to form is hydrocarbon penetration from nearby gas and oil accumulations so that their amounts could provide their complete connection with the sulphate ions. This condition is true for the Ciscarpathians. The vertical migration of hydrocarbons and chemical elements from depths along faults into the sulphate-carbonate unit provoked a number of reactions in them with native sulphur and an assemblage of accompanying minerals as end-products.

In recent years scientists have concentrated on the sulphur content of oil and gas and the possibility of sulphur extraction from them. Oil is a complex solution of several hundred organic compounds, and its composition may vary widely from pool to pool. Oil sulphuring is a primary process that takes place during oil formation in an oxygen-free environment with unsaturated hydrocarbons, complex ethers and hydrosulphide and sulphide ions. Its essence is the formation of stable cyclic sulphur-bearing hydrocarbons (thiophanes). In the USA, the annual production of native sulphur extracted from oil during its cleaning is in excess of 600 thousand tonnes.

The problem of sulphur extraction from gaseous hydrocarbons has risen during the last 15-20 years, after a discovery of major natural gas deposits in the USSR, Canada, France and other countries. The production and processing of hydrogen sulphide-bearing gases is now an industry of its own value in many countries. Illustrative in this respect are two deposits, the Orenburgskoe, USSR, and Lacque, France. The latter, the largest deposit in Europe, has been exploited since 1957. The gas contains as much as 17% hydrogen sulphide to produce over one million tonnes of sulphur a year. This amount can satisfy France's need for sulphur. The gas from the Orenburgskoe deposit contains up to 4.5% hydrogen sulphide.

The World of Minute Minerals

Clay minerals are the smallest representatives of the mineral realm, frequently less than 1 μm in size. These are very fine-grained hydrous silicates (silicic acid salts) with a layered structure. The scientists concerned with clay and clay minerals are up against several problems. These problems are not only their origin and distribution in the Earth's crust but also their relationships to oil, coal, sulphur, iron ores and other valuable minerals.

Petroleum geology is deeply concerned with clay and clay minerals. Compounds very similar in composition to petroleum are derived with passing time and under definite conditions from organic matter disseminated in clays, this mainly consisting of extinct remains of tiny organisms. These compounds are later removed from clays to concentrate in more porous rocks—sands or fractured limestones—where oil pools are just formed. The role of clay minerals in transformation of disseminated organic matter into compounds akin to petroleum in composition is unclear even now. Some believe that clay minerals are catalysts; they accelerate the transformation but do not participate in it. Others think that these minerals not only participate actively in the conversion of organic compounds but change themselves at the same time, somehow activizing organic matter changes. Still others deny at all any participation of clay minerals in organic matter transformation. Clay rocks are least permeable; they tightly plug oil and gas pools, preventing them from destruction. And the oil recovery itself greatly depends on the amount and composition of clay minerals.

Clay minerals are very sensitive to the physicochemical environment. A disturbance of the equilibrium at once causes their conversion to compounds stable under new conditions. These minerals are hence indicative of the character and intensity of processes. That is why the role of clay and clay minerals in the formation of sulphur bodies causes interest. These minerals participate in the generation of primary (earthy) sulphur concentrations, and sulphur crystals and aggregates arise only after their squeeze from these concentrations. Clays reliably cover sulphur bodies.

Geologists of different specialities try to reconstruct the past of the Earth, its organic and inorganic world. This complicated problem cannot be solved without a comprehensive study of mineral material, in particular clays and clay minerals, occurring in sediments of different geological epochs.

Clay minerals have two types of atom disposition in the crystal lattice: tetrahedral and octahedral. In the tetrahedral type, four oxygen atoms are arranged at equal distances, as if at the vertices of four equilateral triangles, about a silicon atom. The other type is an octahedron with faces of equilateral triangles. The vertices of the triangle are occupied by oxygen atoms or hydroxyl groups (OH) and the centres of octahedra, by atoms of aluminium or iron, magnesium, zinc, chromium and other elements. Combined together, the tetrahedra produce tetrahedral nets and octahedra, octahedral ones. Each clay mineral is composed of different net combinations. Thus a combination of an octahedral net with a tetrahedral one produces the structure of the mineral kaolinite, whereas that of two tetrahedral nets with an octahedral one in-between, the structure of montmorillonite and hydromica. The crystalline structure of halloysite does not completely resemble that of kaolinite despite their compositions being identical, except for the two water molecules present in the former. It is made up of kaolinite sheets with oriented water molecules in-between.

The structure of a clay mineral determines all of its properties. Thus kaolinite has a stable structure: its octahedral and tetrahedral nets are strongly connected with one another. It does not expand in water. The structure of montmorillonite is less stable. While it is in water, it expands several times, because water penetrates between the sheets in montmorillonite and push them apart, increasing the total volume. Montmorillonite can be dehydrated and then hydrated again, while halloysite dehydration is irreversible. The replacement of some elements by others in the octahedra and tetrahedra of montmorillonite affects perceptibly its stability. After expansion in water, clay changes easily its shape on mechanical action, that is becomes plastic. One and the same mineral can expand differently. Thus sodium montmorillonite expands much more than calcium montmorillonite.

Kaolinite, montmorillonite and hydromica are principal clay minerals. The first place in amount is taken by kaolinite (kaoline, or porcelain earth, is pure white kaolinite; refractory clays can also contain nearly 100 % kaolinite). Bentonites, or bleaching earth, consist mainly of montmorillonite, and thanks to it they have striking adsorption properties and expand well. Hydromicas are less abundant. In addition, varieties are known intermediate between montmorillonite and hydromica. These are mixed-layered, having intermediate properties. Their structure contains both montmorillonite and hydromica parts. Each clay mineral has its own structural type and crystal lattice. They are determined rather accurately by X-ray analysis, namely by the Debye method or by diffractometry.

Clay has been known since times immemorial. People knew how to make extremely simple pottery from clay as early as approximately 30 thousand years ago. Also, our distant ancestors used clay widely in construction. It gradually entered into the everyday life of people, and its application expanded steadily. Clay appears to have been the most important aid to ancient man; it was used to manufacture nearly all domestic objects. In addition, clay pottery is considered to be the most convincing proof of a settled way of human life. Some ancient peoples even related their origin to clay and believed that it was god's gift. Sumers' zikkurates, statuettes of the Mexican god Ketsalcoatl, posthumous masks of the first pharaohs, which were compared to gods by Egyptians—all of them were made out of clay. The most ancient inscriptions (cuneiform, on clay plates) has until recently been considered to be sumerian, the oldest plates being 2.5 thousand years old. Recently, however, scientists have found clay plates in south-western Syria with letters 5000-5500 years old. Even books were written on clay plates. We say about the most ancient library in the world. It belonged to the Assyrian king Ashurbanipal (7th century B.C.) and numbered more than 30 thousand clay plates. The first notebook was a plate of moistened clay. A text was written on it with a sharpened goose pen or reed stick by Urartians, Egyptians and Phinicians. Many knows of cliff drawings made 20 thousand years ago, but not all know that they were made with clay paints, as in the famous Kapovaya Cave, Southern Urals. The drawings made on cliffs with clay paints were prototypes of later frescos.

Clay with sand and straw has been used since long ago as a building material in the form of bricks. One of the most ancient and lofty constructions made of clay is the temple complex in Tel El Obeid, Mesopotamia. It was built approximately three thousand years B.C. Babylon was also constructed from clay. The majolica from Samarkand has been famous since the times of Timur, i.e., since end of the 14th century. Objects made out of bright different-coloured clay with coarse-grained crock, coated with enamel, became known far outside the city. Thus the Samarkand medrese Bibi-Khanym is still astonishing with its variable mosaics and non-fading bright colours of blue, turquoise, black, green and purple.

As mentioned above, a mixture of sand, clay and straw was the groundmass of bricks called saman. Many instances of saman culture are known. Nowadays, saman brick is popular in the USA. Thick walls of this brick have been found to be much more effective than conditioners.

Clay is part of porcelain, which first appeared in China more than 1300 years ago. A porcelain cup once cost the amount of gold exceeding the volume of the cup.

Fragments of clay dishware are a valuable finding for the archaelogist who tries to reconstruct the history of an extinct people. Variously shaped, coloured and ornamented pots, jars, vases, sculptures and other articles are evidence for its culture and way of life. Centuries passed, civilizations arose and disappeared, but clay objects has survived until our days.

These wonderful properties of clay minerals were used by ancient architects for building the famous Egyptian pyramids. Thus, Cheops' pyramid is built of 2300 thousand blocks each weighing, on average, 2.5 thousand tonnes. Hence the weight of the whole pyramid is 5750 thousand tonnes. How was it possible to transport so huge stone blocks? Even modern powerful mechanisms cannot do this. It has been found that clay helped in this, more correctly a clay suspension, which greatly reduces friction. The suspension was poured on the ground in front of the block that was pulled with ropes and the block moved forward with a relative ease. In this way these blocks were transported from quarries. The ancient Greek frescos show scenes of transport of giant statues and obelisks. You can see on them many people harnessed into special sleighs. You can easily see figures of workmen pouring a clay suspension under the runners of sleighs so that friction is reduced.

Use was made of clay not only for building but also for food. A cream made of kaolinite and deer milk was a real delicacy for some peoples of Siberia and the Far East. Edible clay is sold in markets in Iran; clay from Giveh and Magellat is here preferable. It is a rich white mass sticking to the tongue like halva. A special dish—alipa, a mixture of wheat and marl (clay-carbonate rock) coming from near Napoli—was common in Italy early in this century. Certain kinds of white, blue and greenish clay are delicacies for the natives of some regions of Africa, Australia and ocean islands. Clay "dishes" are considered to be stimulating and medicinal. Initial promising results have recently been achieved in using certain clay as food for livestock and poultry. Clay is occasionally utilized as a fertilizer.

A few people know of coins made of clay. They were manufactured in Germany between 1914 and 1924. These unusual coins were made at the Meissen factory in limited series.

Clay minerals have a wonderful property: they can concentrate and retain energy from the environment. The Soviet scientists N.V. Belov and V.I. Lebedev have shown that the weathering that produces clay minerals is accompanied by solar energy absorption; therefore, the energy reserves early in the weathering are less than at its final stages. Thus one can assume that hydromica has the lowest energy stores, montmorillonite has stored somewhat more energy, and kaolinite has the greatest stores. This feature of clay minerals explains the wide occurrence of hydromica.

The life on Earth is extremely closely connected with clay. Based on the evidence obtained by Soviet geochemists, American scientists have found a confirmation of a hypothesis according to which the origin of life was favoured by clay properties. They have found that clay minerals not only accumulate but also transfer energy. Since it is released by radioactive decay and other processes, clay may become a peculiar "factory" producing an inorganic material necessary for complex molecules to form. The simplest living organisms might have originated on the Earth from such molecules thousands of millions of years ago.

The crystal lattice of clay minerals is far from being ideal. Various defects are normally found in it. They have created conditions for energy storage in minerals throughout thousands of years. The point is that high-energy electrons are caught temporarily where the crystalline structure of clay minerals is disturbed. Crystal lattice defects store information that corrects the course of chemical reactions ultimately responsible for the origin of initial organisms. The British scientist G. Kern-Smith, who put forward this hypothesis, suggests that clays in the coastal strip of ancient oceans were ideal for various chemical processes to occur. He believes that inorganic "proto-organisms" derived from clay not only served as materials for the molecules of living organisms, for instance amino acids, but could participate in their evolution.

According to N.V. Belov and V.I. Lebedev, however, clay mineral transformation in marine sediments progresses in the direction opposite to that under continental conditions. It is accompanied by energy release rather than absorption. So we express some doubt concerning G. Kern-Smith's hypothesis.

Proceeding from the non-ideal crystalline structure of clay minerals, scientists then found that clay was a catalyst for some chemical reactions and even could "selfreproduce". Reproduction of the crystalline structure of clay minerals was observed by the West German scientist A. Weiss.

Clay minerals have sorption properties; they can hold cations and even molecules of other substances on their surface and between sheets. The minerals of the montmorillonite group sorb the greatest number of cations. But the sorbed cations stay very loose in the lattice of clay minerals and so can easily be replaced by other cations. These minerals are effective ion-exchange materials.

That montmorillonites can adsorb various compounds is used to advantage in purifying petroleum products, different oils and other products. This valuable property was noted long ago. Thus the capability of montmorillonite clay to adsorb aromatic stuffs has been utilized in India since ancient times. A specific perfumery industry even arose in the country. One of its hubs is in a village in Uttar Pradesh. The settlers of the village lay disks of burned clay on the ground at the time of the hot season, in May and June, when the air is saturated with the aromatics of tropical flowers and grasses. The disks are gathered and put into a device for distillation just before the rainy season. Light products are caught in a collector by sandal oil and then dissolved in alcohol. The perfumery obtained in this way are called "matti ka ottar", earth perfumes.

The therapeutic properties of natural sorbents have been known for a long time. These include a participation in the control of ionic equilibrium in the digestive tract and in the removal of various harmful substances concentrating in the bodies of human beings. Sorbents can exert a strong influence on microorganisms, promoting the development of some species and suppressing others. Thus, clay minerals enhance anaerobic fermentation and, at the same time, suppress fungal flora.

Finally, clay is the best filler of pills; it levels out the action of strong medicines.

Clay Minerals from Sulphur Deposits

Clay minerals are invariably found in sulphur deposits, but they have yet been studied inadequately. We characterize clay and clay minerals at two Ciscarpathian deposits, the Rozdol'skoe and Podorozhnenskoe, montmorillonite being the major and hydromica the minor mineral.

Montmorillonite, hydromica. Clays have been noted at the sulphur deposits of the Ciscarpathians throughout the entire section of the productive unit, from gypsum to limestone-overlying sediments. Dark-grey and dark-green, intricately curved layers of clay material, probably squeezed out of the anhydrite groundmass during secondary processes, are common at grain boundaries in gypsum and anhydrite. In the limestone, clays occur in two quite distinct complexes that differ in attitude, mineral composition and formation time. The clays of the first complex lie as thin (0.3 to 1.5 m) interbeds in sulphurated and nonsulphurated limestones. These interbeds are compact, grey to bluish grey and black. The dark clay colouration is due to pigmenting substances (organic matter and pyrite) syngenetic to clay minerals. The weathered rocks show variegated clay, which is grey with red patches. Uniform, horizontally stratified clay with a disturbed initial structure (crumpled) predominates in the layers between ore zones. The clay is stratified due to the presence of sand layers and, more seldom, of some plant remains. Native sulphur concentrations often occur along the bedding. This clay has a patterned microstructure due to the oriented arrangement of small scales of clay minerals. Such a structure is characteristic of marine and fresh-water sediments laid down under calm conditions.

The clays of the second complex fill karst funnels in the Rozdol'skoe and other deposits. The groundmass of karst infillings consists of dark-grey and dark, vaguely bedded sandy clays generally with a disturbed initial structure. These are mainly consolidated clays with numerous slickensides on planes of bedding and jointing. They display fragmental and cloddy jointing with sharply angular lumps and fragments 1 to 5 cm in size. On weathering, the clays disintegrate readily into acutely angular fragments and form distinct talus slopes. The weathered varieties expand strongly after rains to produce a gel-like mass. With the onset of a dry weather, they dry up rapidly, and abundant salt efflorescence forms frequently on their surfaces. These clays look under the microscope like a monotonous greyish mass showing randomly oriented clay scales. The unpatterned clays may have initially been normally stratified but then, in karst cavities, they may have been stirred up. The dark clay at the bottom of karst cavities often contains interbeds of dense grey clay; when it is air dry, it is cut with knife with difficulty. This clay soaks in water but slowly, and scaly aggregates are gradually shelled off in the form of a cone. The clay contains much impurities with a prevalence of iron sulphide.

The clay unit overlying the sulphur ores is composed of grey and dark clays grading into clay marl. This unit in the Rozdol'skoe deposit is up to 81.1 m thick, the average being 19.3 m. In the Yazovskoe deposit, the thickness of the clay cap increases from south (35-50 m) to north (170-267 m). Ash-grey clay with a bluish tinge predominates in the Rozdol'skoe deposit. When dry, it is scratched easily with a nail, leaving a bright trace. Rather uniform, light-coloured, persistent, thin (0.5-0.7 m) clay interbeds occur in dark clay. The surface of such clay becomes slippery, gelly after rain; the clay dries up in dry weather and desiccates. It contains many needle-shaped gypsum crystals up to 0.7 mm in size, more or less evenly disseminated over the rock.

Besides the gypsum, iron sulphides are

finely dispersed in the clay, as clearly indicated by electron microscopy, and thermal and other analyses. During their growth, gypsum polyhedra push apart rock lumps under the action of crystallization pressure, and the rock becomes foliated. The clay gets wet easily in water to form a cone. But many small grains are left behind, which suggests that soaking is incomplete. A microscopic study of thin sections of supraore clay has shown that it often has a subparallel texture. Clots and flakes are observed at places, as is a felted structure. In transmitted light, the clay matter is coloured brownish-grey and reacts rapidly to polarized light.

The richest, so-called pelitic fractions were used in studying clay minerals. These fractions are known to provide the most complete information about the composition of clay minerals. The investigation results indicate that montmorillonite is a prevailing mineral of clays. It is made up of small particles and their aggregates with the following refraction indices: $n_g = 1.516$ (average) for cream-coloured clay from the supraore unit in the Rozdol'skoe deposit; $n_{g'} = 1.552$ and $n_{p'} = 1.540$ for ash-grey, loose clay. The grey compact clay from karst sediments in the deposit has $n = 1.536$. Pelitic fractions separated from the clay lying among ores in the Podorozhnenskoe deposit have $n_{g'} = 1.521\text{-}1.538$ and $n_{p'} = 1.526\text{-}1.531$. The above evidence shows that all clays correspond to montmorillonite or are similar to it.

Dark-grey hydromica-montmorillonite clay from sinkholes at the Rozdol'skoe deposit are of extreme interest. An amazing mineral assemblage has been found in the large-size (not argillaceous) fractions of the clay. It is composed of native sulphur, often intergrown with calcite; pyrite in small grains and its earthy variety, melnikovite-pyrite; densely disseminated small hauerite crystals, rare manganese sulphide; small magnetite crystals; quartz in variously rounded grains; ilmenite, zircon, biotite, orthite, plagioclases, calcite, rhodochrosite, manganous calcite, gypsum and bits of volcanic glass. Fresh clay also contains the following sulphates easily soluble in water: melanterite, halotrichite, epsomite and others. Most minerals are crystallographically perfect. Especially interesting among them are quite fresh (unweathered) crystals of black mica—biotite—and common rock-forming silicate—plagioclase.

How have they got into the clay? It is known, after all, that biotite and plagioclase are less resistant to weathering than such rock-forming minerals as potassium feldspar and muscovite. It is hard to assume, therefore, that they were transported by the water eroding weathering crusts, which are the basic suppliers of clastics.

The perfect faces of biotite and plagioclase should be attributed to the overall genesis of clays and source areas. All clays in the sulphur deposits of the Ciscarpathians contain volcanic glass, and the clays from other areas, adjacent to Novyi Razdol, volcanic products, and all this suggests that the clay minerals were derived from volcanic ash decomposed under natural conditions.

Ash is known to be transported over great distances; a volcanic ash layer may be as thick as 20 cm at a distance of 400 km from the eruption centre and 5 m within 50 km. Professor D.P. Bobrovnik has found that Tortonian and Sarmatian tuffs and tuffites are widespread not only in the Transcarpathians, where volcanic rocks are common, but also in the Ciscarpathians. They occur here in a prominent belt in the south-western part of the East European platform. We add that the clay from sulphur deposits also contains perfect zircon crystals whose strongly elongated habit makes it possible to correlate them with those from the acid tuffs of the Transcarpathians. All this confirms once more that the montmorillonite clays formed at sites of their occurrence owing to decomposition of volcanic tuffs under condition of halmyrolysis (underwater weathering).

Good preservation of biotite and feldspar crystals in montmorillonite clays is due to their fall from the air as they were transported from the eruption centres of the Transcarpathians. It is quite possible that these minerals were transported in a "shirt" of volcanic glass, which may wholly have become montmorillonite as a result of halmyrolysis.

Probably, the halmyrolysis occurred in a reducing environment. This stems from an abundance in clay of finely dispersed sulphides of iron, occasionally also of manganese. Because hydrogen sulphide played the main role in the formation of these sulphides, we believe that it favours intensive decomposition of ash material to produce montmorillonite.

Montmorillonite is known to form in an alkaline environment. According to G. Millo, the minimum pH of its origin is 7.5. Since the pH of marine water is generally equal to 8, most investigators cast no doubt as to the possibility for montmorillonite to form in sea water. The most important premise for this process is chemical instability of volcanic glass in sea water and a very slow removal of base-rich solutions from where the silicate material is decomposed. But some data point to a more complex mode of origin of bentonite clay. When volcanic ash decomposes, sea water, which contains much sodium, calcium and other cations, receives even more of these elements, all the more so that they become nearly unmovable at a certain depth from the surface of the sediment. As the volcanic ash decomposes, the pH of the environment was reduced to become neutral. This follows from the fact that the clays are saturated with respect to sulphides of iron, more seldom of manganese. The origin of sulphides is related to a hydrogen sulphide contamination of a water reservoir. And although hydrogen sulphide is a poor acid, there is enough of it for the environment to become slightly acid, which favours a stronger decomposition of the volcanic ash.

But when alkaline and alkali-earth cations enter into the solution, its pH rises again and montmorillonite and hydromica are generated. The bentonite clay appears to have formed throughout a rather prolonged period. Rapid conservation of ash material gave rise to tuffs and tuffites. Feldspars and micas are more resistant to weathering than volcanic glass, so they did not change at all during halmyrolysis.

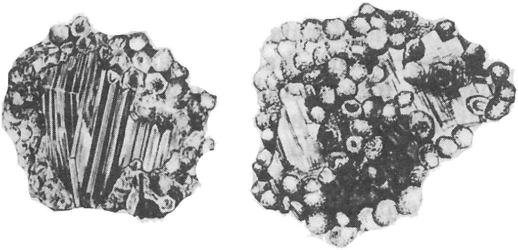
Thus the widespread montmorillonite clays in the sulphur deposits of the Ciscarpathians were derived from halmyrolysis of volcanic ash at places of its deposition; the sources of pyroclastics were volcanic eruptions in the Transcarpathians; active montmorillonite formation in ash was due to hydrogen sulphide-rich water affecting volcanic glass.

Because bentonite clay accompanies the commercial masses of native sulphur so frequently, A.E. Fersman thought of them as sulphur indicative. But why bentonite is associated with the sulphur concentrations of economic value is still unknown. The origin of thick bentonite clay units also needs further elaboration. Note that the bentonite from the sulphur deposits of the Ciscarpathians can be used in building industry, especially if it is mined by open-pit techniques.

Mixed-layer minerals appear to be of double origin. Much of them was directly formed from ash and less from common weathering. Montmorillonite is converted at the Earth's surface to hydromica. In this process, it becomes less crystallized. So the well-crystallized montmorillonite grades into hydromicatized, with little crystallization and an admixture of other clay minerals, more often than not kaolinite.

Halloysite. Another mineralogical mystery refers to the unusual shape of the clay mineral halloysite, which was found in the Gaurdakskoe deposit. Disseminated and banded ores are exposed here. Coarse-grained sulphur in the form of large (upto 4 cm), partially faced phenocrysts associated with granular calcite are well seen in a fine-grained calcite-sulphur groundmass. This aggregate contains large (up to 4 cm) tabular crystals of colourless gypsum. Halloysite in the form of light irregular patches is prominent in areas of oxidized sulphur ores; it fills narrow cracks in sulphur aggregates and is observed in rims, first few millimetres wide, around sulphur phenocrysts. Abundant local segregations of halloysite are restricted to concentrations of lamellar gypsum. In sulphur ores with some clay, halloysite is associated with white powdery alunite.

Halloysite generally occurs in loose, greasy, shapeless porcelain-like masses in interstices between grains of other minerals. It more seldom forms aggregates resembling isometric crystals. Like massive halloysite, they are loose and hollow. These halloysite forms have not been found until recently. Even more seldom is the halloysite as small (tenths of a millimetre) balls. Both "faced" and spherical halloysites arose at the close of sulphur ore



Rounded and "face-bounded" halloysite concentrations

oxidation. In addition, some plates of transparent gypsum contain well-faced halloysite lamellae.

Halloysite is coloured yellowish, bluish, bluish-white, grey and white. The colourless and bluish-grey varieties are cemented with yellowish halloysite. Variegated, clay-like pieces of oxidized sulphur ore with halloysite contain many inclusions of grey-brown hydroxides.

Under the microscope, immersed halloysite is seen as irregularly shaped grey or colourless particles, 0.001 to 0.005 mm in size, with blurred outlines. Their refraction index on two axes is difficult to determine. The birefringence is often very low. So only one, mean refraction index can be measured, and it varies between 1.536 and 1.554.

Much is unclear in the origin of "faced" halloysite aggregates. In all probability, this shape is a product of physicochemical and mechanical transformation of pelitomorphic (very fine-grained) halloysites. Their thin sections not infrequently show a texture of clear-cut polygonal areas closely adjacent to one another. Limited zones of light-coloured halloysite are within the polygons which are frequently separated by thin cracks. These textures are due, on the one hand, to concentrating recrystallization of the halloysite precipitate and, on the other, penetration, along weakened zones (along polygons), of pore solutions, which bleached and dissolved halloysite on their way. Where this process was most complete, the isolated or poorly cemented angular halloysite segregations look like isometric crystals.

The small halloysite balls may have arisen where the mineral-forming solutions were steadily supplied into cavities in oxidized sulphur ores. Faced halloysite lamellae may have been produced by epitaxial crystallization. This is a regular intergrowth of crystals of different minerals whose lattices or some planar nets and rows are similar. Several hundred epitaxial pairs have been described in the mineralogical literature. The planes of halloysite lamellae are parallel to the substrate of gypsum crystals. These lamellae in gypsum began to grow at active centres—in pits of growth confined to linear defects, boundaries of blocks and other disturbances in the gypsum. The oriented intergrowth of both minerals is due to the presence of similar structural motifs on the intergrowth planes.

The mineral halloysite is derived from rapid accumulation of aluminosilicate material under superficial conditions. In the oxidation zone of the Gaurdakskoe deposit, the halloysite was formed from sulphate-bearing solutions produced by oxidation of the native sulphur affecting aluminium-rich rocks (clays and easy-soluble carbonates containing little clay). The alkalis were either removed or included in alunite. The halloysite and alunite formed in the following way:

$$3KAl_2(OH)_2[AlSi_3O_{10}] + 2H_2SO_4 + 10H_2O \rightarrow$$

$$\rightarrow \underbrace{3Al_2(OH)_4[Si_2O_5]}_{\text{halloysite}} \cdot \underbrace{2H_2O + KAl_3(OH)_6[SO_4]_2}_{\text{alunite}} +$$

$$+ K_2SiO_3 + 2Si(OH)_4$$

The combined formation of halloysite and alunite under the action of sulphate-bearing solutions on the hydromica clay was described by the Bulgarian geochemist Kh. Karanov.

Clay Minerals Derived from Underwater Weathering

In the discussion concerning halmyrolysis, we meant the origin of minerals on the floor of the Miocene sea several tens of millions of years ago. But is this process now active under similar geological conditions? Yes, it is, and it proceeds rather vigorously. This is confirmed by studies on volcanic material (basalts, volcanic glass) in the central and north-western Pacific. The mechanical, chemical and biochemical transformation of volcanic rocks leads to an origin of quite an interesting mineral assemblage. The newly formed minerals reflect an overall tendency for a natural system (rock—minerals not at equilibrium between one another) to come to a thermodynamic equilibrium under certain physicochemical conditions. Some of them can be called protominerals—the initial phase of relevant minerals.

Oceanic basaltic volcanism delivers into the sedimentation zone considerable amounts of hyaloclastics—various-size fragments of glassy rocks. Basaltic hyaloclastics change rapidly. Volcanic glass—a magmatic melt that solidified on the ocean floor in the form of amorphous glass almost without other minerals—is altered most readily and replaced by secondary products. The most unstable mineral is olivine. Glass and olivine are replaced by kaolinite, montmorillonite, hydromica and chlorite.

Altered basalt was raised from a depth of 2 km in the north-western Pacific, and a white, sour cream-like protokaolinite mass, with a refractive index of 1.56, flew freely out of the caverns in this basalt. An identical protokaolinite develops after black basaltic glass. As the mineral is drying, it interlocks tightly with the rock. Powdery coatings and crusts of kaolinite were noticed on the basalts at some places in this region. In some samples, this mineral enriches only one zone distinguished by a white colour against a background of basalt and glass. The kaolinite is fine-grained, greasy. Only one index of refraction, equal to 1.562-1.564, can be measured for it. Associated with montmorillonite and hydromica.

Montmorillonite and its mixed-layer varieties with hydromica are most common minerals of ocean-floor rocks. Two mineral varieties have been distinguished: one was derived from underwater weathering of basaltic glass, the other formed under the effect of hydrothermal solutions on basalts. The former is paragenetic with zeolites—specific tectosilicates of the ocean floor and the latter with acute rhombohedral calcite. The hydrothermal montmorillonite is well crystallized and produces yellow fine-grained aggregates with distinct boundaries with other minerals. The montmorillonite after volcanic glass is also fine grained. But its colouration changes from white to yellow and from dark yellow to grey brown, depending on the amount of iron. It shows an aggregate polarization under the microscope, so only one refractive index, varying from 1.5 to 1.6, is measured.

The hydromica of the ocean floor is a scarce newly formed mineral. Its small amounts are associated with the fine-grained montmorillonite. Chlorite together with montmorillonite has been found in orange-coloured powdery aggregates developing after glass and dark-coloured minerals, as well as small bluish-green clumps in disintegrated basalt.

Hisingerite—partly recrystallized hydrated iron-magnesian substance amorphous in X rays—develops after olivine and basaltic glass. Coloured yellow, orange or red brown macroscopically and in transmitted light; some varieties has a peculiar bronzy colour. Hisingerite is semitransparent or translucent. The refractive index varies between 1.46-1.48 and 1.58-1.61 and is often different even in one grain, not only in one sample. An increase in refractive index is due to an enhanced iron oxide content of material. In crossed nicols, hisingerite is isotropic but sometimes has an abnormal birefringence, owing to residual stresses caused by crystallization. It can be confused with montmorillonite, but the latter is always greasy and soft when damp, like butter. We have earlier described hisingerite in alteration products of andesite volcanism in the Sea of Japan. So we can conclude that hisingerite was formed on an extensive scale at the time of underwater weathering of hyaloclastics near eruption centres.

The studies have shown that montmorillonite and its mixed-layer varieties are most stable and widespread minerals in the products of underwater weathering of volcanic materials in the Ciscarpathians and on the Pacific floor. The amount of montmorillonite on the ocean floor rises rapidly in areas of hydrothermal activity marked by intense calcite mineralization.

In the ocean, basaltic hyaloclastics change rapidly with the formations of not only montmorillonite but also hisingerite. No hisingerite has been found in Miocene rocks of the Ciscarpathians. But it doesn't mean that it couldn't have been originated on the floor of the Miocene sea very early in alteration of volcanic material. It could have been converted into montmorillonite with passing time.

The mode of origin of kaolinite is still unknown. Interestingly, this mineral was found only in altered basalts dredged from the spreading zone—a zone of building aside of the ocean floor owing to squeezing out of viscous material and its spreading over the floor.

Conclusion

The origin of minerals present in sulphate-carbonate rocks is still puzzling in many respects. There is an urgent need for further studies on pelitomorphic calcite to which native sulphur from the Ciscarpathians is genetically related. Its composition and properties, the conditions leading to its origin and concentration, and the reasons for its enrichment in light carbon isotope are still to be elaborated. Why calcite crystals of such a specific shape are found here and in no other place of the world, must also be answered.

The demand for natural raw materials will increase in the foreseeable future. Sulphur will not only lead to the development of the chemical industry but will also be used widely in construction. The nature of native sulphur is complicated. Recent data on the mineralogy and geochemistry of sulphur cannot always be explained by the existing concepts. Further progress in science will undoubtedly reveal new properties of sulphur and associated minerals and, thus, will greatly expand their field of application.

Clay minerals play a major role in the formation of many mineral deposits. The discovery of this fact is in line with such remarkable geological discoveries of recent decades as the spreading of the ocean floor and huge concentrations of nonferrous metals in manganese nodules. Clay minerals are rightly considered to be most sensitive to the physicochemical environment. Their role in mineral formation has been described in sufficient detail in numerous publications issued in the USSR and abroad. The clay minerals derived from underwater rock weathering are an interesting subject for further study. It has been found that volcanic glass gives rise to protokaolinite—a phenomenon that is new and of great interest in general to the mineralogist. But the nature of the conversion of volcanic glass to other minerals on the ocean floor still remains a mystery.

Humankind is far from knowing everything about our planet. Puzzles still exist in any field of investigation, as is to be expected. Rather it is their absence that would be a surprise. Modern mineralogy is striving to understand everything, to explain all mysterious and magical phenomena, to benefit from the use of what was created by Nature. There is no doubt that even if this or that piece of knowledge cannot be applied to practice, they could be of great importance tomorrow in solving the quite perplexing problems that still remain. There is no material created by either Nature or human beings that cannot be used for the benefit of humankind.

The objective of these investigations conducted by the author was to explain the origin of an interesting mineral assemblage in sulphate-carbonate rocks. An assessment of the role of the environment in the formation of minerals, their physicochemical transformation under natural conditions, which is of great theoretical significance in gaining an insight into crystal processes was attempted. The book describes minerals of special scientific and technological importance and addresses some problems in geochemistry that are related to mineralogy at the present stage of its evolution.

This book was written in the hope that the readers themselves will come to the conclusion that mineralogical puzzles are always next to us and that they are keen to deserve interest of inquisitive investigators.

Nature has bestowed all of the colours and their varying shades to minerals. Some of the minerals described above have been used for a long time or can be utilized as beautiful decorative stones. And the durability of these objects made from ornamental stones depends not only on their internal structure, i.e. on the degree of interaction between the molecules and atoms, but also on the environment, i.e. on its acidity-alkalinity and redox potential.

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